5-2017

EVALUATION OF ELECTROCOAGULATION FOR CHLORIDE AND AMMONIUM REMOVAL FROM THE REJECT BRINE EFFLUENT PRETREATED BY SOLVAY PROCESS

Miada Abubaker Ali

United Arab Emirates University

College of Engineering

Department of Chemical and Petroleum Engineering

EVALUATION OF ELECTROCOAGULATION FOR CHLORIDE AND AMMONIUM REMOVAL FROM THE REJECT BRINE EFFLUENT PRETREATED BY SOLVAY PROCESS

Miada Abubaker Ali

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering

Under the Supervision of Professor Sulaiman Al-Zuhair

May 2017

Declaration of Original Work

I, Miada Abubaker Ali, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Evaluation of Electrocoagulation for Chloride and Ammonium Removal from the Reject Brine Effluent Pretreated by Solvay Process*", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Sulaiman Al-Zuhair, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

Student's Signature: _____ Date: 21/5/2017

Approval of the Master Thesis

This Master Thesis is approved by the following Examining Committee Members:

1) Advisor (Committee Chair): Professor Sulaiman Al-Zuhair
   Title: Professor
   Department of Chemical and Petroleum Engineering
   College of Engineering, UAE University
   Signature _____ Date 21/5/2017

2) Member: Professor Nayef Ghasem
   Title: Professor
   Department of Chemical and Petroleum Engineering
   College of Engineering, UAE University
   Signature _____ Date 21/5/2017

3) Member (External Examiner): Professor Eric D. van Hullebusch.
   Title: Professor
   Department of Environmental Engineering and Water Technology
   Institution: IHE Delft Institute for Water Education, The Netherlands
   Signature _____ Date 21/5/2017

This Master Thesis is accepted by:

Dean of the College of Engineering: Professor Sabah Alkass

Signature _____ Date 24/5/2017

Dean of the College of Graduate Studies: Professor Nagi T. Wakim

Signature _____ Date 24/5/2017

Copy 9 of 10

Advisory Committee

1) Advisor: Professor Sulaiman Al-Zuhair

Title: Professor

Department of Chemical and Petroleum Engineering

College of Engineering, UAE University

2) Co-advisor: Professor Muftah Hassan El-Naas

Title: QAFCO Chair Professor

Gas Processing Center

College of Engineering, Qatar University

Abstract

Excessive use of desalination, due to the increase in fresh water demand, results in large productions of reject brine. Therefore, the development of an efficient treatment process of the reject brine becomes vital. The Solvay process is one of the main treatment technologies, wherein NH_3 is introduced to convert soluble Na^+ into insoluble $NaHCO_3$. However, in this process, Cl^- is not removed and NH_4^+ is introduced, and therefore electrocoagulation has been proposed for their removal. The experiment was designed using Minitab with different initial concentrations of chloride (7400 – 32600 mg/l), current densities (0.033 - 0.2 A/cm^2) and temperatures (3.2 - 36.8°C). It was found that both percentage and rate of removal increased with the increased in temperature and current density, and the decrease in initial concentration of the ions. For example, at 20°C and initial concentrations of 14250 mg/l and 20000 mg/l for NH_4^+ and Cl^-, respectively, increasing the current density from 0 to 0.2 A/cm^2 resulted in increasing in the removal percentages from 12.5 to 66.7% and from 3.55 to 28.4% for NH_4^+ and Cl^-, respectively. At 0.1167 A/cm^2 and initial concentrations of 14250 mg/l and 20000 mg/l for NH_4^+ and Cl^-, respectively, increasing the temperature from 3.2 to 36.8°C, resulted in increasing in the removal from 42.9 to 72.4% and from 21.8 to 29.8% for NH_4^+ and Cl^-, respectively. However, at 0.1167 A/cm^2 and 20°C, increasing the initial concentration of Cl^- from 7400 to 32600 mg/l resulted in decreasing in the removal from 56.9 to 45.3% and from 30.3 to 25.6% for NH_4^+ and Cl^-, respectively. The results were fitted into model equations (14 and 15), which were validated against an independent experimental point not used in their development. The selected points were the middle points for the independent variables for central composite design for current density (0.1167 A/cm2) and initial concentrations of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, but for temperature, the selected point was the high-level point for the independent variables for central composite design (30°C). At this condition, the removals of ammonium and chloride were found to be 71.55% and 26.88%, respectively.

Keywords: Desalination plants, reject brine, electrocoagulation reactor, Solvay process, ammonium and chloride removals.

Title and Abstract (in Arabic)

تقييم التخثر الكهربي لإزالة أيونات الكلورايد والأمونيا من المحلول الملحي المركز الناتج من عملية السولفاي

الملخص

الاستخدام المفرط لتحلية المياه، بسبب زيادة الطلب على المياه العذبة، يؤدي إلى إنتاج كمية كبيرة من المياه المالحة. ولذلك، فإنه من المهم تطوير تقنيات فعالة لمعالجة المياه المالحة. عملية سولفاي هي واحدة من التقنيات الرئيسية المعالجة ، حيث يتم ضخ NH_3 لتحويل Na^+ الذائب إلى $NaHCO_3$ الغير قابل للذوبان. ولكن مع ذلك فإن استخدام عملية السولفاي لا ينتج عنه إزالة الكلورايد وبالإضافة إلى ذلك فإن كمية الNH_4^+ تزداد، وبالتالي تم اقتراح التخثر الكهربي كطريقة لإزالة الأمونيوم والكلورايد من المحلول الملحي المركز الناتج من عملية السولفاي. استخدمت تراكيز أولية مختلفة من الكلوريد (7400 - 32600 ملغم / لتر)، و كثافات كهربائية مختلفة (0.033 - 0.2 أمبير / سم^2) ودرجات حرارة مختلفة (3.2 - 36.8 درجة مئوية). وقد وجد أن كلا من النسبة المئوية ومعدل الإزالة قد ازداد مع زيادة درجة الحرارة و الكثافة الكهربائية ، ومع انخفاض التركيز الأولي للأيونات.

على سبيل المثال فقد تبين أنه عند 20 درجة مئوية، و 20000 ملغ / لتر كتركيز أولي من الكلورايد و14250 ملغ/ لتر كتركيز أولي من الأمونيوم ، فإن زيادة الكثافة الكهربائية من 0 إلى 0.2 أمبير / سم^2 تؤدي إلى زيادة نسبة الإزالة من 12.5 إلى 66.7٪ ومن 3.55 إلى 28.4٪ من الأمونيوم والكلورايد، على التوالي. وعند الكثافة الكهربائية 0.1167 أمبير / سم^2 ، و 20000 ملغ / لتر كتركيز أولي من الكلورايد و14250 ملغ/ لتر كتركيز أولي من الأمونيوم ، فإن زيادة درجة الحرارة من 3.2 إلى 36.8 درجة مئوية، تؤدي إلى زيادة نسبة الإزالة من 42.9 إلى 72.4٪ و من 21.8 إلى 29.8٪ من الأمونيوم والكلورايد، على التوالي. وعند الكثافة الكهربائية 0.1167 أمبير / سم^2 ، و درجة الحرارة 20 درجة مئوية، فإن زيادة التركيز الأولي

من الكلورايد من 7400 إلى 32600 ملغ / لتر، يؤدي إلى انخفاض في نسبة الإزالة من 56.9 إلى 45.3٪ و من 30.3 إلى 25.6٪ من الأمونيوم والكلورايد، على التوالي. تم استخدام برنامج Minitab 17.0 وتم اجراء 20 تجربة لدراسة تأثير درجة الحرارة، والتركيز الأولي للكلورايد والأمونيوم، والكثافة الكهربائية على نسبة إزالة الكلورايد والأمونيوم من محلول السولفاي. تم ادراج النتائج في برنامج الMinitab وعليه تم الحصول على المعادلة النموذجية التي تمثل العلاقة بين المتغيرات والنتائج، وللتأكد من صحة هذه المعادلة تم استخدام تجربة مختلفة عن ال 20 تجربة التي استخدمت لوضع المعادلتين (14 و15). هذه التجربة المستقلة هي عبارة عن كثافة الكهربائية بمقدار0.1167 أمبير / سم^2، و درجة حرارة بمقدار30 درجة مئوية، و 20000 ملغ / لتر كتركيز أولي من الكلورايد و14250 ملغ/ لتر كتركيز أولي من الأمونيوم. وفي هذه التجربة فقد وجد أنه 71.55% من الأمونيوم و 26.88% من الكلورايد قد أزيلت.

مفاهيم البحث الرئيسية: محطات تحلية المياه، المياه المالحة المركزة، تخثر كهربي، عملية سولفاي، إزالة الأمونيوم والكلورايد.

Acknowledgements

Sincere thanks are expressed to my advisor Prof. Sulaiman Al-Zuhair for his guidance, support and constructive feedback throughout my thesis study. I am grateful for the time he has taken to guide and support me.

My thanks extended to my co-advisor Prof. Muftah El-Naas who helped me along the way. Also, special thanks are extended to all members of the Chemical and Petroleum Engineering Department at the UAE University for assisting me during my studies and research and the Library Research Desk for providing me with the relevant reference material.

Finally, I would like to thank Dr. Hussain Awad, Dr. Kilani Ghoudi, Eng. Sami Abdulla, and Eng. Essa Lwisa for their help and support. Special thanks go to my parents, brothers, and sister who helped me along the way.

Dedication

This thesis is dedicated to my beloved parents and family, who supported me all the way since I began my postgraduate study. I would like to extend this dedication to my thesis advisor whose motivation and encouragement was a great source of knowledge and experience

Table of Contents

List of Tables

List of Figures

List of Abbreviations

CCD	Central composite design
CD	Current density (A/cm^2)
DoE	Design of experiments
EC	Electrocoagulation
I	Current
IC	Ion chromatography
M_W	The substance molecular weight (g/mol)
MED	Multiple Effect Distillation
MSF	Multi-Stage Flash
R^2	Determination coefficient
RO	Reverse osmosis
t	The operation time (s)
TWh	Terawatt-hours
z	The number of electrons which involved in the reaction

Chapter 1: Introduction

1.1 Overview

In many regions, the water resources, including oceans, rivers, lakes and underground aquifers are under stress due to excessive withdrawal from surface waters, excessive withdrawal of water from underground aquifers, pollution of fresh water resources, inefficient use of freshwater (Fry and Martin, 2005). In human consumption, the main water demand comes from urban communities, requiring water for drinking, drainage and sanitation. It is expected that the urban population will grow to 6.3 billion people in 2050 compared with 3.4 billion in 2009 due to migration from countryside to the city and population growth. Between 1990 and 2012, there is about 1.7 billion people who do not have access to improved sources of drinking water and tap water (Water for a sustainable world includes data and indicators annex for water and energy, 2015). The shortage of water supplies for drinking and irrigation purposes is already a very serious problem in the Middle East and several other countries in South East Asia and Latin America and severe water shortages may occur in many countries of the European Union and the northern Mediterranean by 2020 (Le Dirach et al., 2005).

In addition to the water shortage, the main water resources, such as surface and ground waters, are being constantly polluted from industrial effluents as well as other natural processes (Palaniappan, United Nations Environment Programme, Division of Environmental Policy Implementation, and Pacifica Institute, 2010). Therefore, the treatment of wastewater has become an important issue. As a result, there is a need for developing effective and inexpensive techniques to treat different

water sources, and seawater desalination has become an important way to secure freshwater supply for many countries, including the Gulf States (Dawoud, 2005).

Processes are specifically designed to remove unwanted elements, such as iron, manganese, ammonium, fluorides, chlorides, nitrates, heavy metals and others from water. Traditional technologies implemented to produce drinking water include coagulation, flocculation, decantation, sand filtration, activated carbon and ion exchange. New technologies include membrane technologies such as microfiltration, nanofiltration, ultrafiltration and reverse osmosis. There are several disadvantages of using the membrane technologies instead of the traditional technologies. These disadvantages include that the drop in flow as the membranes becoming clogging with the time, the sensitivity to operating parameters and feed characteristics, constant cleaning and parts replacement requirements and high fixed costs (Esfahani et al., 2014).

1.2 Relevant Literature

1.2.1 Desalination

Desalination has become an essential source for production of drinking water. More than 11,000 desalination plants are in operation throughout the world (Cotruvo, 2005). Desalination is a process that separates the saline water into two streams, the distillate which is the fresh low-salt concentration, and the reject brine stream which is the high-salt concentration stream (El-Naas, 2011b). Currently, the global production of about 65.2 million m^3/d of desalinated water involves the use of at least 75.2 TWh per year, which equals about 0.4% of the global electricity consumption (Isaka, 2012). Large financial resources for research and training in

desalination have been invested. Desalination can be achieved either by physical filtration (membrane separation) processes such as Reverse Osmosis or by thermal desalination, such as Multi-Stage Flash (MSF) and Multiple Effect Distillation (MED). These method are the most commonly used in desalination, especially in the Gulf and Middle east areas (El-Naas, 2011b), and are described in sections 1.2.1.1 – 1.2.1.3.

Distillation processes produce about 50% of the worldwide desalination capacity, and 84% of this is produced by MSF technology. Most MSF plants have been built in the Middle East, where energy resources have been inexpensive and plentiful (Shatat and Riffat, 2012).

1.2.1.1 Multi-Stage Flash (MSF)

The Multi-Stage Flash Distillation process consists of "flashing" portions of water into steam, and this is repeated in several stages at lower and lower pressures. Each stage contains a heat exchanger and a condensate collector. Seawater enters the tubes of the heat exchangers, and the condensation of the vapor that is created at each stage is what heats the seawater. After passing through the heat exchangers, seawater enters the brine heater, where it is heated to the highest temperature that the plant allows. After that, it enters the first stage where the pressure is decreased to just below the vapor pressure of the water. This forces a portion of water to be immediately boiled and evaporated, which is then condensed as it enters the tubes of the heat exchanger, which is collected in a tray. The freshwater is then cooled as it is transported so that the excess energy can go into heating the seawater that first enters the plant, which is called heat-recovery (Cheah, 2000), as shown in Figure 1.1

Shuweiat plant is the largest MSF unit in the United Arab Emirates with a capacity of 75,700 m^3/day (Khawaji et al., 2008).

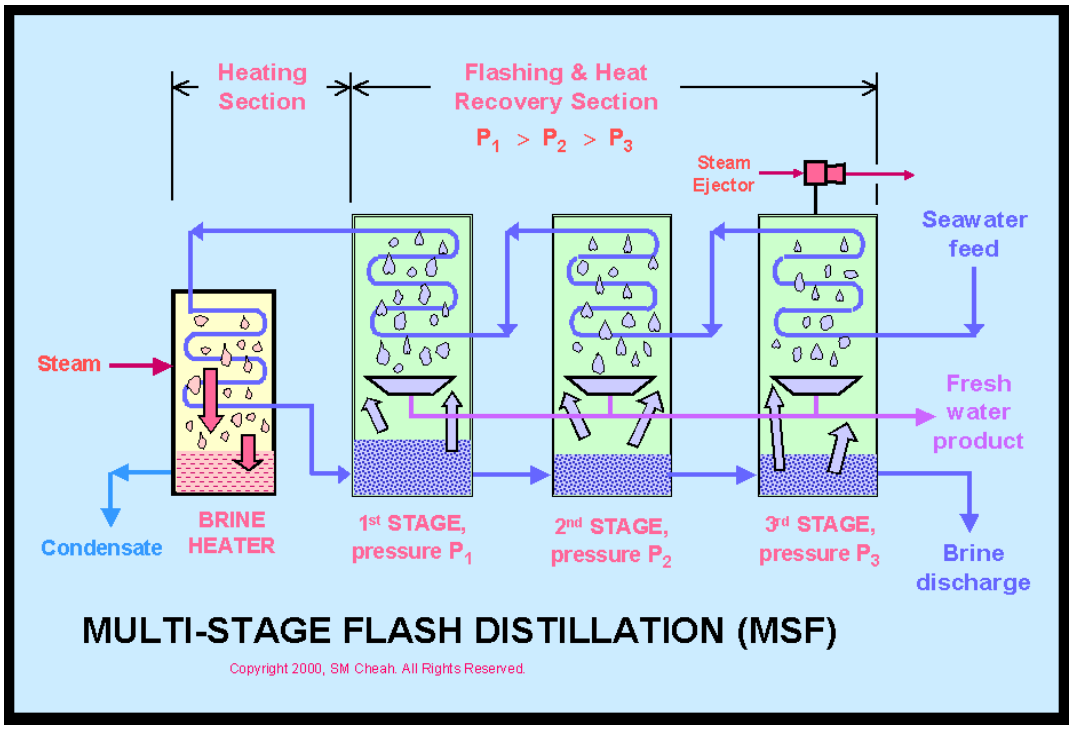

Figure 1.1: Schematic diagram of Multi-Stage Flash (MSF) (Cheah, 2000)

1.2.1.2 Multiple Effect Distillation (MED)

The Multiple Effect Distillation (MED) is categorized as the oldest desalination method, which is thermodynamically very efficient (Sayyaadi et al., 2010). Without supplying additional heat after the first effect this process allows the seawater feed to undergo a multiple boiling. A series of evaporators called effects or "stages" is achieved, as shown in Figure 1.2. At reducing pressure and temperature, from a stage to the next, a repetition of evaporation and condensation takes place. The need to save energy was the basis for the development of this multi-stage process, whereby more equipment is required in order to reduce the overall amount and cost of energy consumed. In most cases, the process involves 2-4 stages (Semiat, 2000). The most

interesting part about MED is that each stage reuses energy from the previous stage in order to heat the incoming brine. When water evaporates in one stage, that steam flows through tubes to the next stage. Thus the heat from that evaporated water is used to heat and evaporate even more water at the next stage (Cheah, 2000).

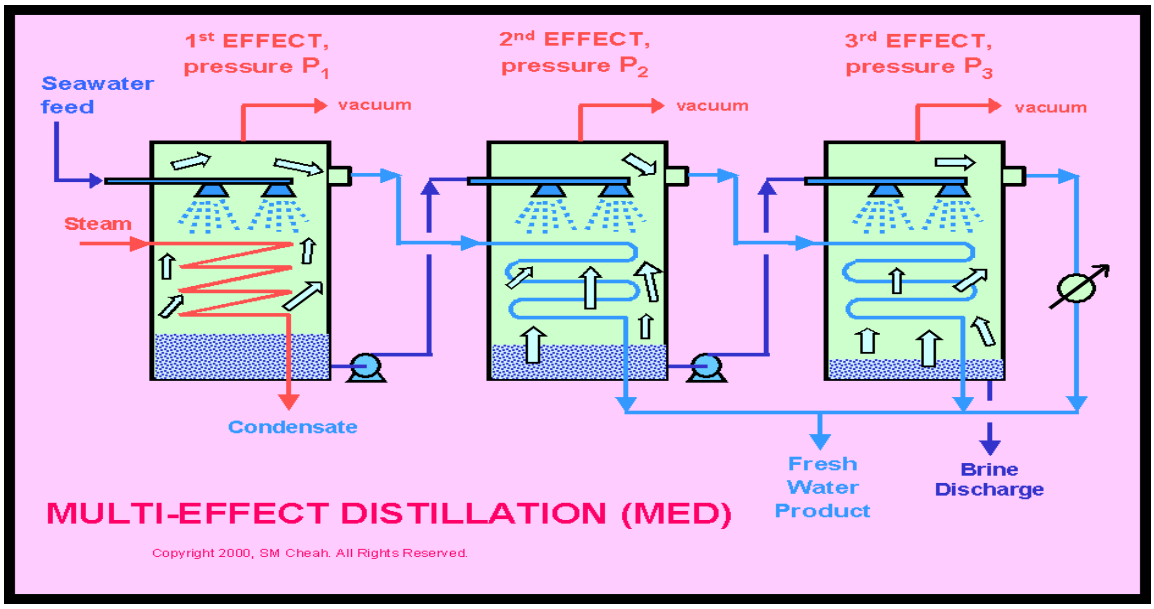

Figure 1.2: Schematic diagram of Multiple Effect Distillation (MED) (Cheah, 2000)

1.2.1.3 Reverse Osmosis

Reverse Osmosis is a non-thermal process where no heating or phase separation is required. RO is a pressure-driven process, with the pressure used for separation by allowing fresh water to pass through a membrane, leaving the salts behind; to overcome the osmotic pressure as shown in Figure 1.3. This process consists of: feed water pre-treatment unit, high pressure pumping unit, membrane separation unit and permeate post-treatment unit. The seawater flows through different stages to reach the desired quality. Firstly, the seawater flows through screens to remove the solid waste, and then it passes through the quality filters for further cleaning. After that,

the pressure of the pretreated feed water is increased so that it becomes suitable for the membrane. Only the molecules passes though the membrane, while the dissolved salts are retained (Sauvet-Goichon, 2007).

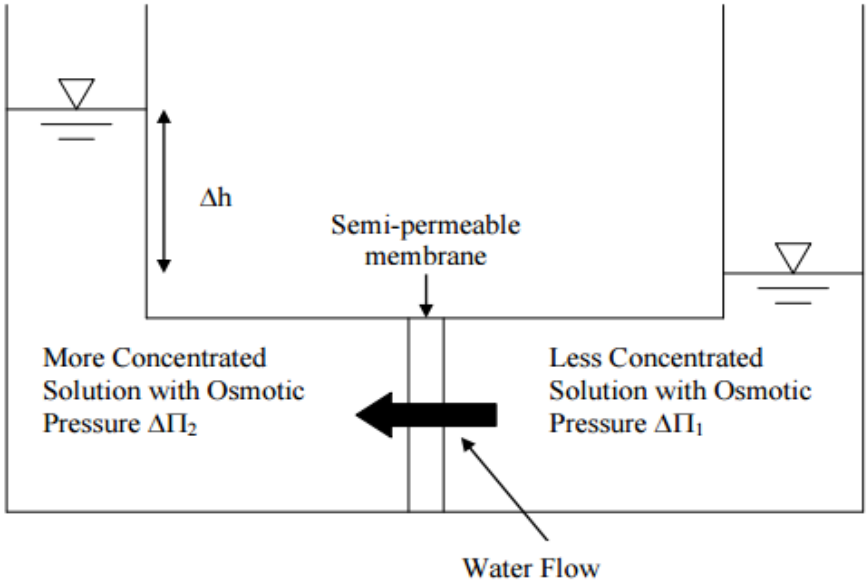

Figure 1.3: Schematic diagram of Reverse Osmosis (Tanuwidjaja, 2002), where the water only passes though the membrane after overcoming the osmotic pressure, while the dissolved salts are retained

1.2.2 Reject Brine Management

In spite of the development of new and highly efficient desalination processes little improvements have been reported for handling and managing the waste by product reject brine. For every 1 m^3 of desalinated water, it is evaluated that an equal amount of the reject brine is generated (El-Naas, 2011a). In the year of 2015, the global production of desalinated water was 86.55 million m^3/day (Voutchko, N., 2016). The main environmental challenges to most desalination plants are the management or the disposal of the concentrated brine. The cost of the brine disposal ranges between 5% and 33% from the total cost of the desalination process (Pérez-

González et al., 2012). There are limited options for the treatments which include: discharge to wastewater treatment plants; deep well injection; land disposal and evaporation ponds (El-Naas et al., 2010). The common process to deal with this product is to discharge it back into the sea, which as a result will affect the aquatic life and the quality of the sea water in the long run (El-Naas et al., 2010). Different factors play important roles in the selection of the best disposal method. These factors include the reject brine composition, the acceptance of the public, the amount and the quality of the brine, the availability of the location where the brine will be discharged to, the capital and the operating costs of the amount of the brine that must to be treated before disposing in an acceptable level (El-Naas, 2011a). The most common techniques for the treatment of the reject brine are presented in sections 1.2.2.1-1.2.2.4.

1.2.2.1 Discharge to wastewater treatment plants

Mixing the high salinity brine with a water body reduces the salinity of the brine stream. But a salinity assessment impact must be done on the receiving stream because this improper dilution of the brine could cause significant marine pollution (Ahmad & Baddour, 2014). In order to determine the cost of discharging the reject brine, there are different factors that need to be taken into consideration. These factors include the cost of the construction and operation, the cost of the transportation of the reject brine from the desalination plant to discharge point, and the cost of monitoring the effects of disposal of the reject brine into the water body (El-Naas, 2011a).

The main disadvantages of discharging into the water body are the high concentration of the chemicals that could decrease the level of the dissolved oxygen

available for the marine organisms. In addition, there might be some harmful chemicals inside the reject brine such as chloride and hydrogen sulfide, which need to be treated before disposing (El-Naas, 2011a).

1.2.2.2 Deep well injections

For the disposal of industrial, municipal and liquid hazardous wastes, deep well injection is often considered (El-Naas, 2011a). This method is usually more expensive compared to the discharge to surface water; because in the latter method long brine transport pipelines are not required. There are some considerations that must be taken with the deep well injection of the brine, such as the selection of the site, done after a complete geological studies, the capital and the operating cost associated with the injection through a deep well, possible leakage in the casing of the well due to the corrosion and protection of the groundwater resources from pollution (Muniz and Skehan, 1990).

1.2.2.3 Evaporation ponds

The most common method for brine disposal from inland desalination plants is the evaporation ponds. There are some advantages of using this process, such as low maintenance and operation cost, easy to construct and no mechanical equipment requirements (Ahmed et al., 2000). On the other hand, there are many drawbacks of using evaporation ponds, which are including the contaminations that might happen due to the dissipation of the reject brine into the soil and groundwater and also the need of large area of the ponds. In addition, the evaporation rate strongly depends on the effectiveness of ponds, which in turn depends on the weather conditions (El-Naas, 2011a).

1.2.2.4 Solvay

Ernst Solvay was the first one who developed and successfully uses the Solvay process in 1881. It is initially developed for the manufacture of sodium carbonate, where concentrated brine is contacted with ammonia and carbon dioxide to form soluble ammonium bicarbonate, which reacts with the sodium chloride to form soluble ammonium chloride and a precipitate of sodium bicarbonate according to the following reaction (El-Naas, 2011a):

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl \quad (1)$$

The ammonia plays an important role in the reaction of the Solvay process where it buffers the solution at a basic pH and increase the precipitation of sodium bicarbonate. The most important intermediate product in the Solvay process is the sodium bicarbonate ($NaHCO_3$) where the success of the Solvay process depends on the solubility of the sodium bicarbonate ($NaHCO_3$). The solubility of $NaHCO_3$ must be as low as possible to achieve high conversion. To limit or reduce its solubility it is very important to optimize the factors that could achieve the lowest solubility (El-Naas, 2011a). Increasing the concentration of ammonium bicarbonate would result in increasing the concentration of (HCO_3^-) which would force the equilibrium in the reactions to the left and thus lower the solubility of $NaHCO_3$.

$$NH_4HCO_3\ (a) \leftrightarrow NH_4^+ + HCO_3^- \quad (2)$$

$$NaHCO_3\ (a) \leftrightarrow Na^+ + HCO_3^- \quad (3)$$

The aim of the Solvay process is the formation of sodium carbonate, but for brine management the aim is to convert water-soluble sodium chloride into insoluble sodium bicarbonate that can be removed by filtration (El-Naas, 2011)

In this thesis, the optimum condition for the Solvay process was used where the experiments are done in the semi-batch mode. The highest sodium removal of 33.0% and the best CO_2 capture of 86.2 % were obtained under specific conditions. The optimum CO_2 capture efficiency and ions removal was found to be at temperature of 19.3^oC, gas (10% CO_2 and 90% Air) flow rate of 1.544 L/min, and 3.3NH_3:1NaCl molar ratio (Mohammad, 2015a).

In industrial application, the first step is passing the ammonia gas through the concentrated brine to have the ammoniated brine, and then the carbon dioxide is bubbled through the ammoniated brine to form ammonium chloride and sodium bicarbonate (El-Naas, 2011a).

There are some advantages and disadvantages of using the Solvay process. The advantages includes that less electric power is required, the corrosion problem is less, low grade brine is used, there will be no problem of disposal of co-product and does not require ammonia plant while the disadvantage of using the Solvay process include that the Solvay products cannot be return back to the sea water because it affects the aquatic life and the ammonia released in the air during the process (Dutton, 2014).

1.2.3 Electrocoagulation Process

Electrocoagulation (EC) was first patented in the United States in 1909, but because it needed a relatively large capital investment and expensive electricity

supply at that time the electrocoagulation wastewater technologies did not find a wide application worldwide. But with the increase of the regulation of waste water discharge quality and the standards of the drinking water supply, electrocoagulation process regained its importance during the past two decades (Hamdan, 2014).

Electrocoagulation is the process that neutralizes the charges of suspended solids, which results in a gelatinous large mass that is easy to settle or trapped in a filter. It is difficult to remove particles of sizes less than 10 microns. Coagulants could be produced using the EC process mostly from either iron or aluminum electrodes (Engelhardt, 2010). EC is a complex process, where chemical and physical processes occur simultaneously. The metal ions, generated from the sacrificial metal anode once the current passed through the electrodes, cause destabilizing of the suspended particles and breaking of emulsions. After this process is done, a flocculation is formed by the aggregation of the destabilized particles, and a sludge is created, which can be removed by sedimentation, flotation or filtration process (Mollah et al., 2004).

The electrocoagulation reactor, in its simplest form, consists of an electrolytic cell with at least one anode and one cathode, as shown in Figure 1.4. Once external power source is connected, an oxidation corrosion reaction takes place at the anode, while the cathode is passivated (Mollah et al., 2001).

There are many advantages of the EC, which include: 1) produces low amounts of sludge, 2) bubbled gasses are produces which causes a floating of the pollutants (suspended solids) at the top of the solution, which can be easily collected, 3) high efficiency because Flocs are formed that are larger and more stable than flocs formed in chemical coagulation, 4) the smallest colloidal particles are removed because the collision becomes faster when the current is applied, which causes the formation of

the coagulant (Moussa et al., 2016), 5) small equipment sizes (Mook et al., 2012). On the other hand, the disadvantages of the EC include: 1) passivation of electrodes because of the presence of oxides and of precipitation layers on the electrode surfaces, 2) the dissociation of the electrodes, and hence regular replacement of the electrodes is required which lead to additional costs (Moussa et al., 2016).

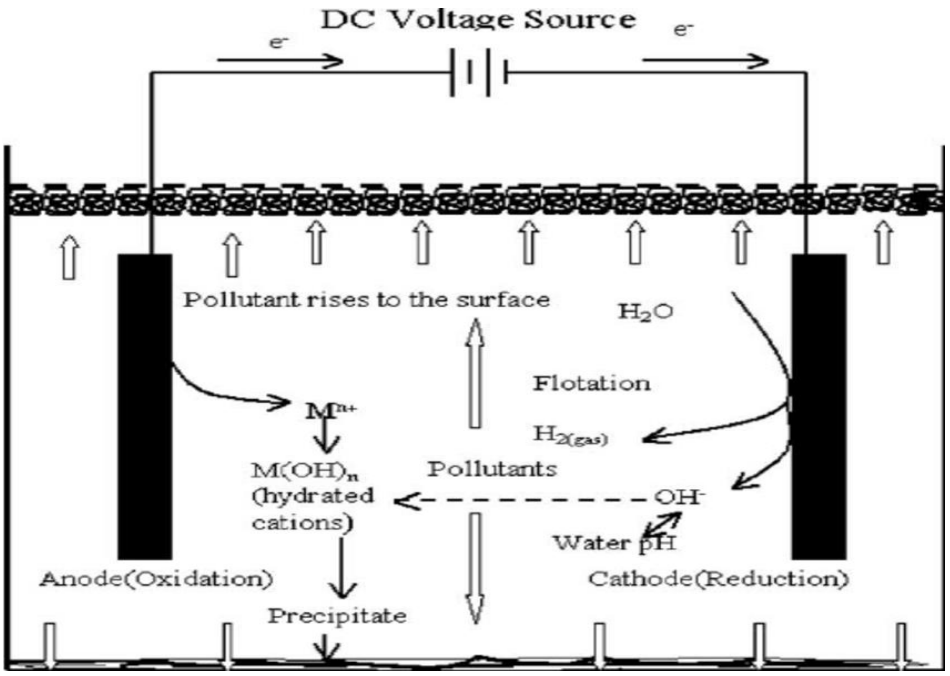

Figure 1.4: A schematic diagram of an electrocoagulation cell (Mollah et aI., 2004)

The treatment with this technique is based on destabilizing dissolved or suspended contaminants in the aqueous medium. These contaminants in raw waters and wastewaters are typically colloidal particles, which are in stable situation in the aqueous solutions, making it difficult to remove by sedimentation in a reasonable period of time. This stability comes from the balance between the attractive and the repulsive force. These colloids could be described as microscopic particles, which have at least one dimension in the range of 1 nm to 10 μm, that are dispersed throughout the other substance (Vepsalainen and Valtion, 2012). The charge on the

surface of the particles attract ions on the solution of the opposite charges and repulse ions of the same charges (Vepsalainen and Valtion, 2012). Electrical double layer is then formed due to the separation of charges on the particle surface, as shown in the Figure 1.5:

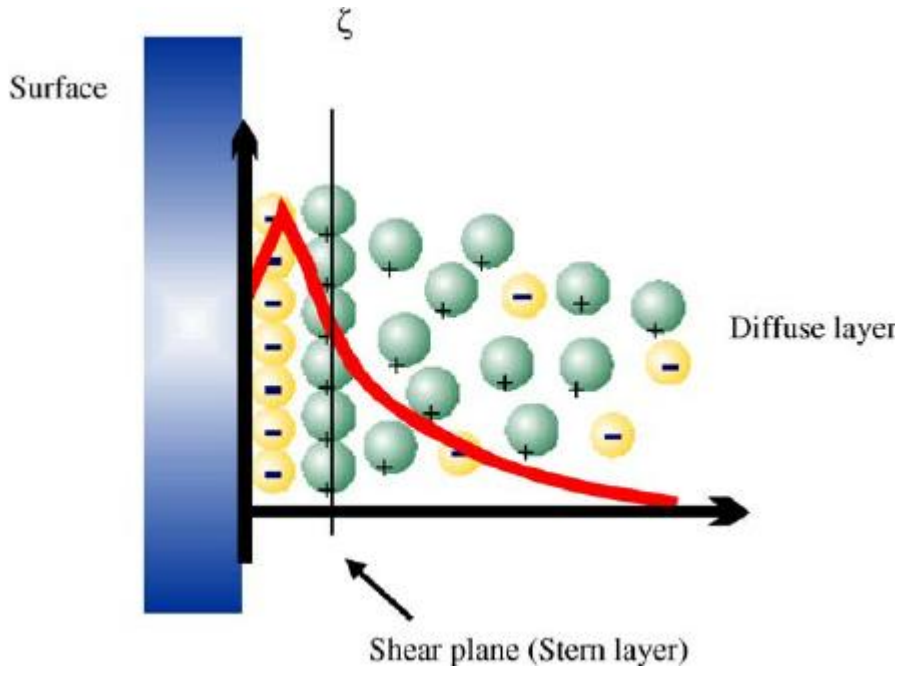

Figure 1.5: Schematic diagram of the electric double layer. The Stern layer of counter ions (layer of bright grey (yellow) ions) that attach to a charged surface. Ion concentrations near the surface decrease further from the surface, thus forming the diffuse layer (Vepsalainen and Valtion, 2012)

In inner region known as stern layer, ions are tightly bound to the surface, whereas the outer layer known as Gouy-Chapman layer are moving under the influence of diffusion (Vepsalainen and Valtion, 2012). On the other hand, a destabilization of the colloids could be achieved when inorganic or organic chemicals added to the solution to decrease the repulsive energy between the particles, where they could be agglomerated to each other in a weak bond and improve the flocculation process.

The reactions at the anode and the cathode could be divided into the main reactions that cause the destabilization of the pollutants and the side reactions, such as the hydrogen formation. Both of the reactions are summarized in section 1.2.3.1:

1.2.3.1 Mechanism of the process

Aluminum and iron electrodes are the most common types which are preferable in the EC (Engelhardt, 2010).

The reactions that takes place in EC have both good and bad effects. The good side of the reactions is that the produced flocculated material can be removed from the water. The adverse side is the deposition of salts on the electrode surface, which may cause deterioration of removal efficiency after long operation. The Fe electrodes could dissolve into divalent $Fe^{2+}$and trivalent Fe^{3+} forms, whereas there is only one form for aluminum dissociation, which is the trivalent form Al^{3+} (Moussa et al., 2016). The anodic equations, which illustrate the dissociation of the iron electrodes into cations, iron is oxidized according to Eq. (4), which is further reacted with OH^- to form $Fe(OH)_n$ is shown in Eq. (5), both equations are illustrated as the following:

$$Fe(s) \longrightarrow Fe^{n+}(aq) + ne^{-1} \quad (4)$$

$$Fe^{n+}(aq) + OH^- \longrightarrow Fe(OH)_n(s)\text{ , where n = 2 or 3} \quad (5)$$

The divalent form of the iron goes through further oxidation to form $Fe(OH)_3$, as shown in Eq. (6) (Moussa et al., 2016):

$$4Fe^{2+}(aq) + 10\ H_2O + O_2(aq) \longrightarrow 4Fe(OH)_3(s) + 8H^+ \quad (6)$$

At the same time at the anode, chlorine gas is produced, and that is the main process for the removal of chloride. The reaction can be represented by the following Eq (7):

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad (7)$$

At alkaline pH and sufficient anodic potential, evolution of oxygen at the anode might also take a place as the following equation (Moussa et al., 2016):

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (8)$$

The cathode electrode dissolution during the EC, results in the formation of ammonia gas as shown in Eq. (9), and that is the main process for the removal of ammonium ion which is the same equation found by Frank Jirsa for the electrolysis of aqueous solutions of ammonium iodide (1950), and also hydrogen gas produced (Picard et al., 2000) at Fe cathode as the following:

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2 \quad (9)$$

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \quad (10)$$

Other electrochemical reactions that could take place in EC are the formation of hydroxides at the cathode as shown in Eqs (11-12):

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \quad (11)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^- \quad (12)$$

Evolve of hydrogen from the anode and cathode, and hydrogen oxides from the cathode explain the slight decrease of the pH, which indicates that the amount of the hydrogen produced was slightly more that the hydrogen oxides which precipitate as $Fe(OH)_n$.

Using the Faraday's law, the amount of metal cations which dissolve at the anode during the reactions can be calculated using Eq (13):

$$m = \frac{I.t.M_W}{z.F} \quad (13)$$

Where, m is the quantity of the metal dissolved (g), t is the operation time (s), Mw is the substance molecular weight (g/mol), z is the number of electrons which involved in the reaction (2 for Fe^{2+} and 3 for Fe^{3+}), F is Faraday's constant (96485 C/mol) and I is the current. However, at basic pH the dissolution of the iron anodes has shown a lower amount than that calculated using the Faraday's law, due to the other electrochemical reactions such as the combination between the ions and the carbonate that may take place.

The highest concentrations of the products are found at the surface of the electrode and decreases from the surface towards the bulk solution. As a result of that, the pH increases at the vicinity of the cathode surface and the vice versa on the anodes where it decreases. When the solubility changes as a function of the pH, a precipitation of inorganic salts on the electrode surface occurred (Hasson et al., 2008).

1.2.3.2 Treatment parameters

The efficiency of the EC for removal of contamination from wastewater is affected by various parameters. These parameters include (Vepsalainen and Valtion, 2012) :

1. The current density: The concentration of the coagulant which is produced by electrolysis on the anodes, is directly proportional to the current density applied.
2. Concentration of the pollutants:

3. Temperature: The formation of the floc, the conductivity and the reaction rates are affected by the temperature.
4. Concentration of the anions: The competing anions can replace the hydroxide anions and can then, effect on the efficiency of the coagulant processes. It was found that the lower the concentration of the anions, the better the removal.
5. Material of the electrodes: such as iron or aluminum, and in sometimes an inert material could be used as the cathode electrode. Most results indicate that iron dissolves as Fe(II) and is oxidized in bulk solution to Fe(III) if there are oxidants, such as oxygen, present in sufficient concentration and pH is alkaline. (Chen, 2004).
6. pH of the solution: Affects the speciation of metal hydroxides in the solution. It was found that the removal efficiency increases when the initial pH of the wastewater increases (Shafaei et al., 2011).
7. Treatment time: The amount of the coagulants produced in the EC process are proportional to the time.

1.2.3.3 Properties of the sludge

Sludge which is produced from the EC is a major challenge, which needs to be treated and to be disposed. It is one of the major cost factors in water and waste water treatments (Gomes et al., 2007). A crystalline phase is produced from the Fe-Fe electrodes such as magnetite, and poorly crystalline phases, such as iron oxyhydroxides and lepidocrocite. The sludge which is produced by the iron electrodes is heavy and produces a compact layer (Emamjomeh and Sivakumar, 2009).

1.2.3.4 Applications of electrocoagulation

EC can be used to treat the wastewater from mining, pulp and paper industries, and metal-processing industries. In addition, it has been applied to treat water containing oil wastes, dyes, foodstuff wastes, suspended particles, chemical polishing waste, organic matter, synthetic detergent effluents and heavy metal-containing solution (Mollah et al., 2001).

Numerous articles were published on EC application on the removal of pollutants from real or synthetic solutions. These studies can be divided into different categories as follows:

1. **Removal of metal ions and/or hydroxides** from synthetic solutions, Wastewaters or ground waters are shown in Table 1.1.

Table 1.1: Recent studies in which EC has been used to remove metal pollutants from water (Vepsalainen and Valtion, 2012)

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References
Cobalt as Co(11)	Synthetic solutions	Al electrodes	Current density, initial pH, conductivity, initial concentration, treatment time	Initial pH has significant effect on removal efficiency. Higher removal efficiency in neutral or alkaline initial pH.	(Shafaei et al., 2011)
Iron as Fe(11)	Fe(11) added into tap water	Al electrodes	Current density, initial concentration, treatment	Practically complete removal with long treatment	(Ghosh et al., 2008)

			time, inter-electrode distance	time and/or high current density	
Mercury as Hg(11)	Synthetic solutions, surface water	Al and Fe electrodes	Current density, Initial pH, treatment time, inter-electrode distance, electrode material	Practically complete removal of mercury. Higher efficiency of treatment with iron electrodes	(Nanseu-Njiki et al., 2009)
Indium as In(11)	Synthetic solutions	Al, Fe and combination electrodes	Initial concentration, electrode material, initial concentration, applied voltage	Highest removal efficiency with Fe- Al electrodes	(Chou et al., 2009)
Manganese as Mn(ll)	Synthetic solutions	Al electrodes	Initial pH, current density, treatment time, anions, conductivity, initial concentration	Improved removal in neutral and alkaline pH. Possible direct reduction at the cathode surface	(Shafaei et al., 2010)

2. **Removals of organic material** from wastewaters or synthetic solutions are shown in Table 1.2:

Table 1.2: Recent studies in which EC has been used to remove organic pollutants from wastewaters (Vepsalainen and Valtion, 2012)

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References

Slaughter-house wastewater, manure	wastewaters	Al and Fe electrodes	Current density, treatment time, initial pH, electrode material	Over 70% removal of COD, color and oil-grease obtained. Highest removal efficiency in acid or neutral pH. Al electrodes are more effective in removing COD and color, whereas iron is more effective in removing oil-grease.	(Yetilmezsoy et al., 2009, Kobya et al., 2006)
Oily waters, petroleum refinery wastewaters	wastewaters	Al, Fe and stainless steel electrodes	Electrode configuration, initial pH, treatment time, electrode material, initial concentration, temperature	Typically, > 90% oil and grease, petroleum hydrocarbons, turbidity and sulfate obtained. Fe electrodes can be more efficient than Al. Removal	(Asselin et al., 2008, Tir and Moulai-Mostefa, 2008, El-Naas et al., 2009)

				increases at lower temperatures.	
Olive mill wastewaters	wastewaters	Al and Fe electrodes	Initial pH, treatment time, current density, supporting oxidants coagulants	Typically, over 70% removal of COD, polyphenols, turbidity, and color. Significantly decreases toxicity of wastewater. Fe can give higher removal efficiency than Al. Oxidants and other coagulants can improve removal.	(Hanafiet al., 2010, Tezcan Un et al., 2006)
Tannery wastewaters	wastewaters	Al and Fe electrodes, stainless steel cathodes	Conductivity, current density, initial concentration, treatment time, electrode configuration	Fe electrodes are more effective for the removal of COD and sulphide than compared with aluminum electrodes. Typically	(Dengil, Kulac, & Ozacar, 2009, Espinoza-Quinones et al., 2009)

				high removal of COD, BOD, TSS, sulphide, oil grease, Cr, Fe and turbidity (80-100%) obtained.	

3. **Purification of surface waters** from natural organic matter, inorganic pollutant or microbes are shown in Table 1.3 (Vepsalainen and Valtion, 2012).

Table 1.3: Recent studies in which EC has been used to remove pollutants from surface waters or groundwater and nutrients from wastewaters

Pollutants	Matrix	Electrode material	Studied parameters	Optimum conditions and notes	References
Boron	Geothermal waters	Al electrodes	Current density, temperature, treatment time	High boron removal efficiency (96%) obtained. Increases temperature increases removal efficiency. Optimal pH is slightly alkaline	(Yilmaz et al., 2008)
Fluoride	Synthetic solutions	Al electrodes	Anions, current density, initial concentration,	Flouride competes with other anions. Sulphate inhibits	(Emamjomeh & Sivakumar, 2009, Hu et al., 2003, Zhu et al.,

			initial pH, flow rate, residence time	localized corrosion of the electrodes. Chloride and nitrate prevent the effect of sulphate and enhance corrosion. Practically complete removal of fluoride possible	2007)
Microorganisms	Synthetic solution	Al, Fe and stainless steel electrodes	Current density, treatment time, electrode material, salinity	Al electrodes were slightly more effective than Fe or stainless steel. Complete removal of microorganisms is possible. Efficiency of the treatment increases with increasing temperature.	(Ricordel et al., 2010, Ghernaout et al., 2008, Uduman et al., 2011)
Surface water, natural organic matter	Synthetic solutions, surface waters	Al and Fe electrodes	Current density, applied voltage, initial	Simultaneous removal of microbes obtained.	(Koparal et al., 2008, Ricordel et al., 2010

			concentration, treatment time, distance between the electrode		
Nitrate	Synthetic solutions	Al and Fe electrodes	Treatment time, current density, initial concentration, initial pH.	Optimal removal at alkaline pH (pH 10-11). Nitrate removal follows first-order reaction kinetics. Over 90% removal can be obtained.	(Lacasa et al., 2011, Emamjomeh and Sivakumar, 2009)

Landfill leachate treatment:

Leachate is usually generated from precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through a landfill (Wu et al., 2004). This leachate is not easy to be treated in a way which satisfies the discharge standards due to composition variations and high proportion of refractory materials (Labanowski et al., 2010).

The efficiency of electrocoagulation in removing ammonia nitrogen (NH_3-N) from leachate has been investigated. The factors affecting the efficiency of removing NH_3-N of the leachate, such as current density, electrolysis time, and Cl^- concentration were considered. The operating conditions with current density of 4.96 mA/cm^2 , Cl^- concentration of 2319 mg/L, operating time of 90 min with Fe electrode gave the highest NH_3-N removal efficiencies of 38.6% (Li et al., 2011). Leachate treatment by electrocoagulation using aluminum electrodes in a batch process; with an initial chloride concentration of 3100 mg/l, pH 9.6, operating time of 30 min and 631 A/m^2 was also tested with various modifications (aeration, and alkalinity addition). The removal of ammonia reached up to 24% (Ilhan et al., 2008).

Removing nutrients from waste water using energy efficient electrocoagulation with an air-breathing cathode

Energy efficient electrocoagulation with an air-breathing cathode are used to remove the nutrients as well as suspended solids and organic carbon from wastewaters using the activated carbon air cathode and a sacrificial aluminum anode, as shown in Figure 1.6. An experiment was done at a current density of 8 A/m^2 and 1.5 cm electrode. A synthetic solution consists of (nitrogen: phosphorus ratio of 1:10 in deionized water) was used to simulate the nutrients. It was shown that using higher

initial nutrient concentrations resulted in lower removal, where the ammonia removals decreased from 93% to 75% when the initial concentration increased from 50 to 500 mg-N/l. Increasing the nutrient concentration caused an increase in the conductivity, and floc was then more readily formed and accumulated at the bottom of the reactor, causing a large local current between the anode and the cathode. As a result more anode mass was consumed to generate precipitates depositing on air cathode, hindering oxygen transfer (Tian et al., 2016).

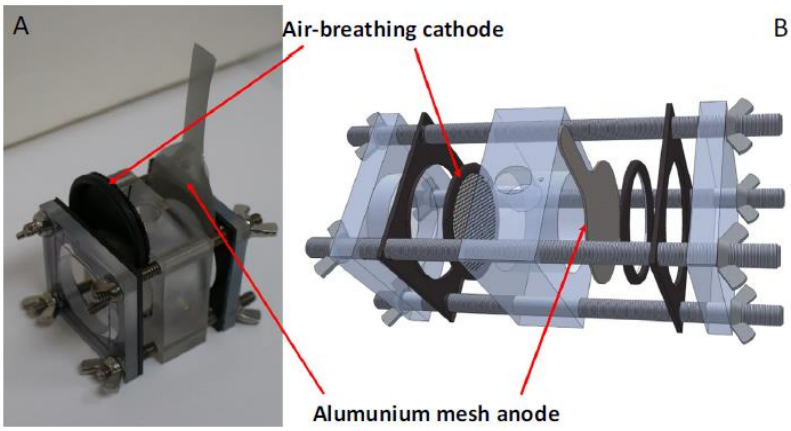

Figure 1.6: (A) Schematic diagram and (B) photo of the electrocoagulation reactor with an air cathode (Tian et al., 2016)

Norcure Concrete Chloride Removal System

The Norcure chloride extraction treatment is a system for electrochemical extraction of corrosive chloride from concrete (Kumar and Singh, 2015). This is the most important techniques to reduce the corrosion problem in the concrete, due to the entry of chlorides which penetrates into the concrete structures due to its porous nature of concrete. Eventually reaching the reinforced steel or rebar. Using EC to remove the chloride, concrete would be saved without any needs to the inconvenience disruption of conventional repair.

This process, shown in Figure 1.7. consists of conductive mesh temporarily mounted on the concrete surface as anode, existing steel reinforcement as cathode and Norcure electrolyte, which is an aqueous pH controlled solution as electrolyte. The current density is typically 1 A/m^2 of concrete surface (Chamber, 2004).

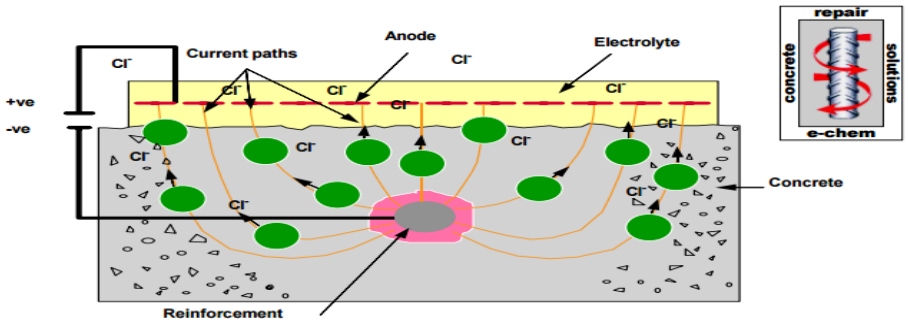

Figure 1.7: Norcure Concrete Chloride Removal System (Chamber, 2004)

EC is used to treat the distillery wastewater using aluminum electrodes. It was found that the optimum pH range from 3.5 to 5 and the maximum percentage of removal of chloride is 37.28% after 90 minutes at 30 volts. Increasing the volts in the electrolytes was found to increase the percentage removal of chloride (Sasane and Korke, 2015). Another study was done for chloride removal using electrocoagulation and it was found that increasing the temperature of the electrolyte solution resulted in increasing the electrochemical chloride removal efficiency (Ueda et al., 2012).

1.2.4 Conclusion Remarks

As mentioned earlier, the Solvay process reduces the salinity of reject brine by precipitating Na^+ ions as $NaHCO_3$. However, the Cl^- ions are kept intact. In addition, the NH_3 needed in the process is dissolved as NH_4^+. The objective of the work is therefore to reduce the concentration of the Cl^- and regenerate the NH_3 from the effluent of the Solvay process by EC, NH_4^+ cannot be dissolved as a salt because it

has a high solubility in water, so it needs to be regenerated as NH_3. EC was selected because it has shown promising results for the removal of dissolved ions. The project looks into optimizing the removal of the ammonium and chloride ions. Effects of temperature, initial concentration and current density on the removal efficiency were tested. Although EC was used separately for the treatment of chloride and ammonium ions as mentioned in the application of the EC, but EC has never been done before for treating the Solvay solution which containing both ions.

Chapter 2: Material and Methodology

2.1 Experimental Apparatus

The electrocoagulation experiments were conducted using Plexiglass jacketed reactor with an internal diameter of 14.5 cm, and a physical height of 14.5 cm. Volume of the treated Solvay solution in each experiment was 500 ml. The reactor was left uncovered to allow the generated gasses to escape. The electrodes were connected to an aluminum strip hanging on the edges of the reactor. Two rectangular iron electrodes were used with dimensions of 13.5 cm x 6 cm. The contacted area of electrodes immersed in the solution was 15 cm^2. The electrodes were placed 8.5 cm apart and were connected to a DC power supply (PE-23005, 2X0-30V/ 5A - 5V/ 3A). Between the electrodes, a mechanical stirrer (RW10R, JANKE and KUKEL, IKA-WERK, Germany) was immersed and used to agitate the solution. The reactor was specially designed and built for this study and was operated in a batch mode. The temperature inside the reactor was controlled by water circulated through the surrounding jacket from a temperature controlled water bath (Model: Julabo F34, Germany). The water entered the jacket from the bottom and exited from the top. A schematic diagram of the batch reactor is shown in Figure 2.1:

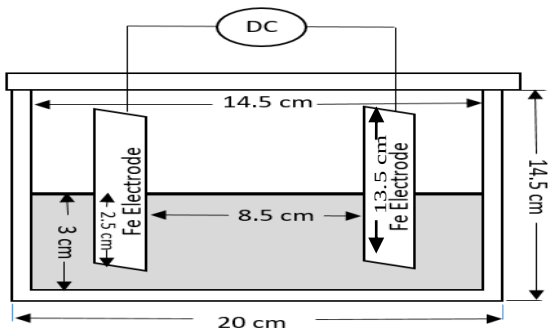

Figure 2.1: Schematic diagram of the batch reactor

2.2 Brine Samples and other Reactants

Ammonium hydroxide aqueous solution (25 wt. % NH_3) and ammonium bicarbonate (purity 99.9%) were obtained from Scientific Progress Medical and Scientific Equipment, UAE. A gas mixture of (10% CO_2 and 90% Air) was purchased from Abu Dhabi Oxygen Company, UAE. Nitrogen-Ammonia Reagent Set, Nessler, was purchased from Concorde Trading Co. L.L.C. UAE. Reject brine samples with salinity ranging between 65,000 and 75,000 ppm were obtained from a local desalination plant utilizing RO desalination process. The average values of the samples were analyzed to determine pH, Na^+, Mg^{2+}, Ca^{2+} and K^+, Cl^- and NH_4^+ concentration, which are presented in Table 2.1.

Table 2.1: Characteristics of the reject brine and effluent from the Solvay process

	PH	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	NH_4^+
Reject brine	9.16	23712 ppm	2794 ppm	762 ppm	1375 ppm	33225 ppm	0
Solvay effluent	9.8	15887 ppm	55.88 ppm	332.2 ppm	141.62 ppm	32600 ppm	17875 ppm
±	0.01	12.2	8.7	4.6	3.1	0.27	0.045

2.3 Experimental Methods

2.3.1 Solvay Preparation

The Solvay solution was prepared at the optimum conditions as described by (Mohammad, 2015b), using 1 liter of the reject brine mixed for five minutes with ammonium hydroxide in a molar ratio of $3NH_3$:1NaCl. The mixture was then fed to a stainless steel jacketed, bubble column reactor, which was operated in a semi-batch

mode (batch for liquid phase and continues for gas phase) at a controlled-temperature of 20 °C. A gas mixture containing 10 vol. % CO_2 in air was bubbled through the reactor at a flow rate of 1 L/min for 6 hours. The composition of the solution at the end of the process is shown in Table 2.1. As shown in the table, although the Solvay process reduced the concentration of Na^+, Mg^{2+}, K^+ and Ca^{2+}, the concentration of Cl^- and NH_4^+ has significantly increased. This effluent is then treated by EC to remove these ions.

2.3.2 Variation of Different Parameters

Different initial concentration of chloride (7400 mg/l, 12500 mg/l, 20000 mg/l, 27500 mg/l, 32600 mg/l) were prepared by diluting the effluent Solvay solution which is 32600mg/l. 500 ml of the Solvay effluent was placed in the batch reactor. Water was circulated through the jacket from water bath set at different temperatures of (3.2°C, 10°C, 20°C, 30°C and 36.8°C). 36.8°C is the maximum temperature that could be handled by the batch reactor used in the experiment, and beyond this temperature a leakage in the reactor happened. Temperature was measured inside the reactor, and was monitored throughout the experiment and it was found that the temperature from the beginning until the end changes maximum ± 5. After the desired temperature was reached different current densities of (0.033 A/cm^2, 0.067 A/cm^2, 0.1167 A/cm^2, 0.167 A/cm^2 and 0.2 A/cm^2) were applied. 0.2 A/cm^2 is the maximum current density that could be applied based on the concentrations that were used in the experiments. Samples were collected every 60 minutes and analyzed for N-NH_4 concentration using Ultraviolet–visible spectrometry (UV) and Cl^- concentration using ion chromatography (IC) (DIONEX ICS-1100, USA). The pH

was continuously monitored throughout the experiment and the pH from the beginning until the end changes maximum ± 1.

2.3.3 Experimental Design

In order to design the experiment, mathematical and statistical techniques are collected to decide the optimum settings for the variables in a definite region of interest which called response surface methodology (RSM) (Khuri, 2003). The important side of the RSM is the design of experiments (DoE) (Ramachandran and Tsokos, 2015). For the physical and numerical experiments these methods were developed. Selection of the experimental points where the response should be evaluated is the main purpose of the DoE. After doing the experiments, the mathematical model which are generally polynomials with an unknown structure that represent the process is constructed and from that an optimal design can be found (Khuri, 2003). Before deciding the main factors, screening experiments are performed to determine the factors that have significant effect of the response. There are different methodologies for RSM such as: a full factorial design which examine all the possible combinations of the variables (Anderson-Cook et al., 2009) and Central Composite Design (CCD) which has a less number of experiments as compared to a full factorial design (Song et al.,2014).

Central Composite Design (CCD) was used to design the experiment. Preliminary study was done to determine the time needed to achieve the maximum removal of ions using the EC process. It was found that most of the drop in ions concentrations took place within the first six hours, and therefore, the duration of the experiments was set to that time. The three major factors, which affect the efficiency

of the removal of ions, were selected to be the temperature, the current density and the initial concentration of the ions. The experimental conditions for central composite design (CCD) runs are presented in Table 2.2.

Table 2.2: Range and level of independent variables for central composite design runs

				Levels				
Factors	Tag	Symbol	Units	-α	-1	0	1	+α
Current density	I	X_1	A/cm^2	0.033	0.067	0.1167	0.167	0.2
Temperature	T	X_2	°C	3.2	10	20	30	36.8
Initial Concentration of Cl^-	IC	X_3	mg/l	7400	12500	20000	27500	32600

2.3.4 Measurement of Different Ions

2.3.4.1 Measurement of Chloride Using IC

Ion Chromatography System with Degas and Chromeleon Software was used to determine the chloride ion concentration. The characteristic of the IC was having the eluent concentration of 4.5 mM Na_2CO_3 and 0.8 mM Na_2HCO_3, with pump flowrate = 0.25 ml/min, suppressor: type = AERS_2 mm, current = 7 mA and column oven temperature = 30°C, it has a column and a column guard with the following specification (Dionex Ion Pac AS 23, 2X250 mm), (Dionex Ion Pac AG 23, 2X50 mm)) respectively.

2.3.4.2 Determination of Ammonium Concentration

The ammonium concentration was determined spectroscopically by adding 3 drops of the Mineral Stabilizer, 3 drops of Polyvinyl Alcohol Dispersing Agent and 1.0 mL of Nessler Reagent set, added in sequential manner to 25 ml sample in a mixing cylinder. Thorough mixing was applied to the sample between each addition. A blank solution was prepared in the same procedure, but using 25 ml of deionized water instead of the sample. The mixtures were allowed to react for 1 min before measurement. The instrument was zeroed using the blank, then the ammonium concentration was determined using the UV spectrometry at a wavelength of 425 nm.

Chapter 3: Results and Discussion

3.1 Effect of the Applied Current

The kinetic removal of NH_4^+ and Cl^- on the percentage removal of NH_4^+ and Cl^- ions was tested at initial concentration of 15593.75 mg/l and 27500 mg/l of NH_4^+ and Cl^-, respectively, and at 30°C. The experiment was done shown in Figures 3.1 and 3.2.

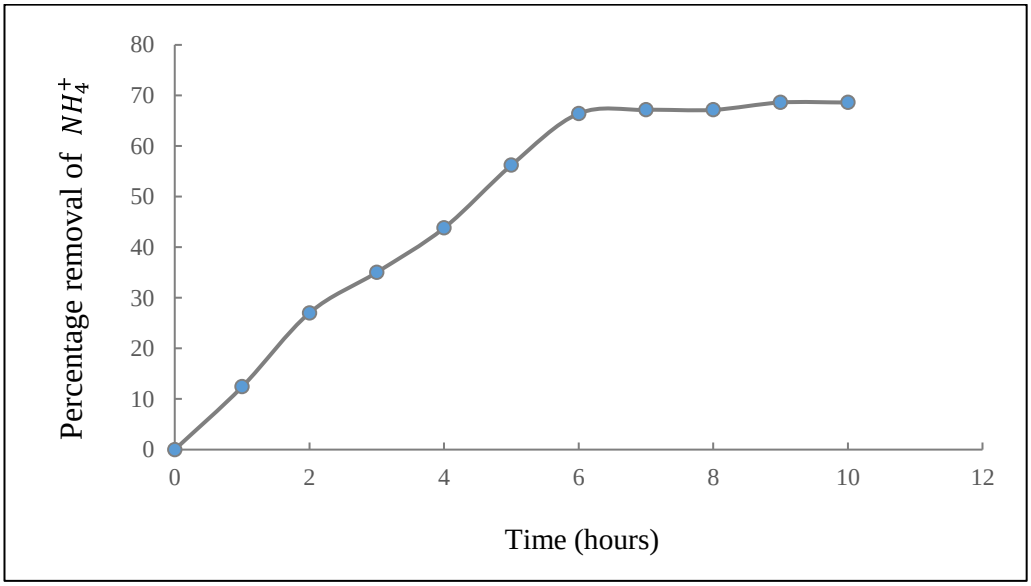

Figure 3.1: Effect of adding current for 10 hours on the percentage of removal of NH_4^+

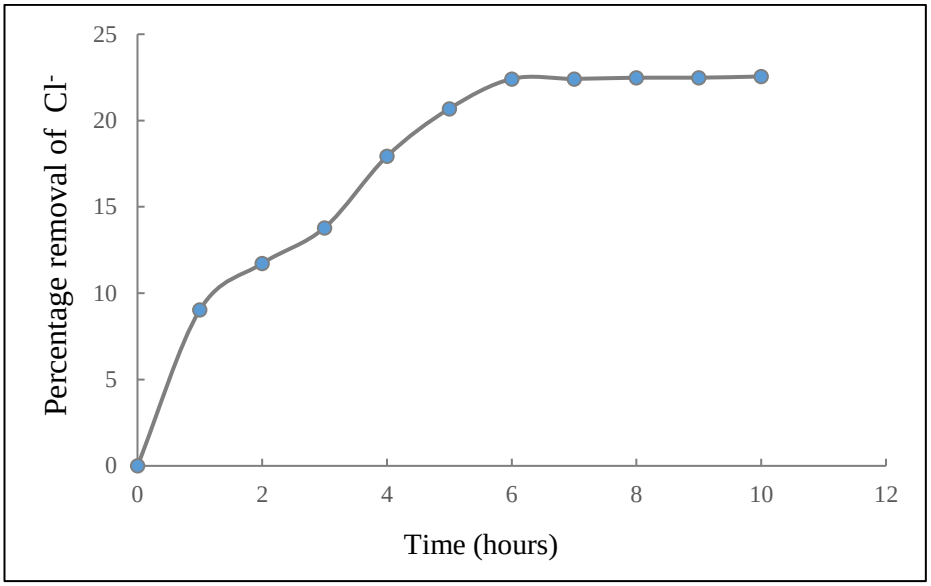

Figure 3.2: Effect of adding current for 10 hours on the percentage of removal of Cl^-

Adding current in the EC cell on the percentage removal of NH_4^+ and Cl^- ions was tested at initial concentration of 14250 mg/l and 20000 mg/l of NH_4^+ and Cl^-, respectively, and at 20°C and 30°C, which represent the middle and high values of the temperature effect (i.e., x_1= 0 and 1). The experiment was done, and the data was found in appendix (A). This was used to determine the percentage removal shown in Figures 3.3 and 3.4.

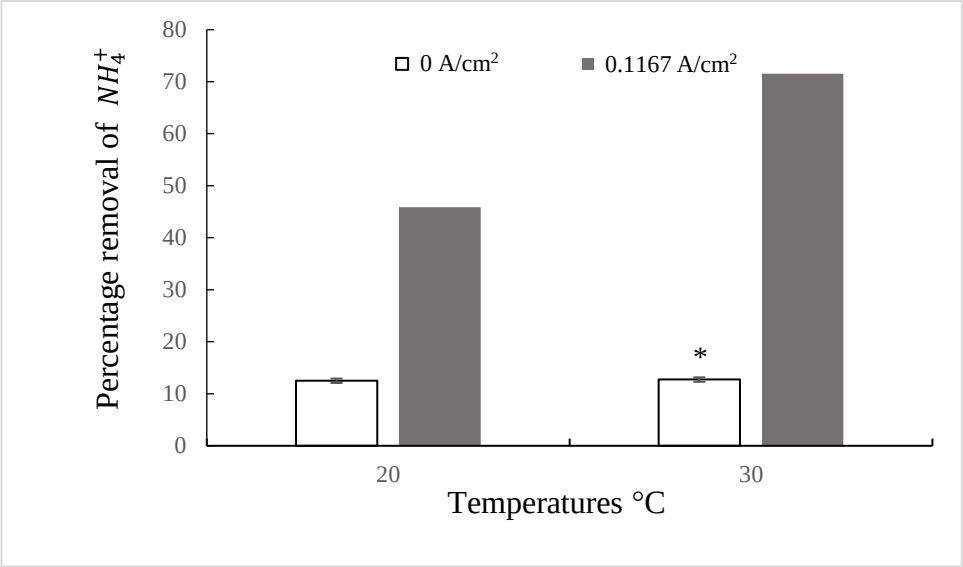

Figure 3.3: Effect of adding current on the percentage of removal of NH_4^+ after 6 hours at different temperatures and an initial NH_4^+ concentrations of 14250 mg/l. * Comparison between the percentage removals without current at 20 and 30°C (p-value = 0.637)

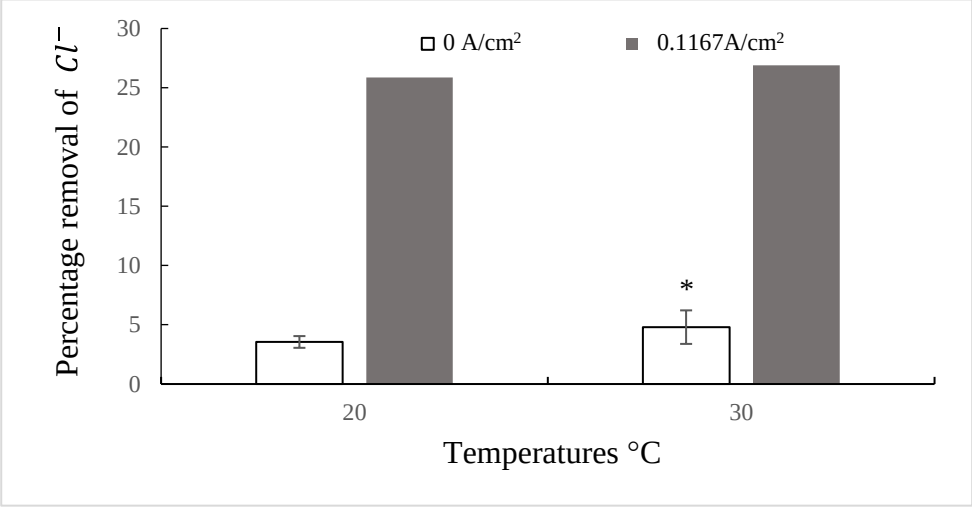

Figure 3.4: Effect of adding current on the percentage of removal of Cl^- after 6 hours at different temperatures and an initial Cl^- concentrations of 20000 mg/l. * Comparison between the percentage removals without current at 20 and 30°C (p-value = 0.359)

As shown in Figures 3.3 and 3.4, when no current was applied very small removals of ammonium and chloride were recorded which was due to evaporation or any other reason, which were 12.5% and 3.55% at 20°C, and about 12.7% and 4.8% at 30°C for ammonium and chloride, respectively. It is clearly seen that increasing the temperature from 20°C to 30°C did not show a significant effect in the percentage removal of both ions, with p-values of 0.637 and 0.359 for ammonium and chloride ions, respectively. Applying a current of 0.1167 A/cm^2 caused a significant increase in the ammonium removal from 12.5% to 45.9% at 20°C, and from 12.7% to 71.55% at 30°C. As for chloride removal, applying a current density of 0.1167 A/cm^2 caused an increase in the chloride removal from 3.55% to 25.87% at 20°C, and from 4.8% to 26.88% at 30°C. These results prove that the removal of ions was solely due to the effect of the electrocoagulation, and any other effect, such as evaporation was minimal even at the higher temperatures in the tested range.

The effect of current density, in the range of 0 to 0.2 A/cm^2, on the percentage removal of NH_4^+ and Cl^- ions was tested at 20°C and initial concentrations of 14250 mg/l and 20000 mg/l of NH_4^+ and Cl^-, respectively. The experiment was done, and the data was found in appendix (A). This was used to determine the percentage removal shown in Figure 3.5:

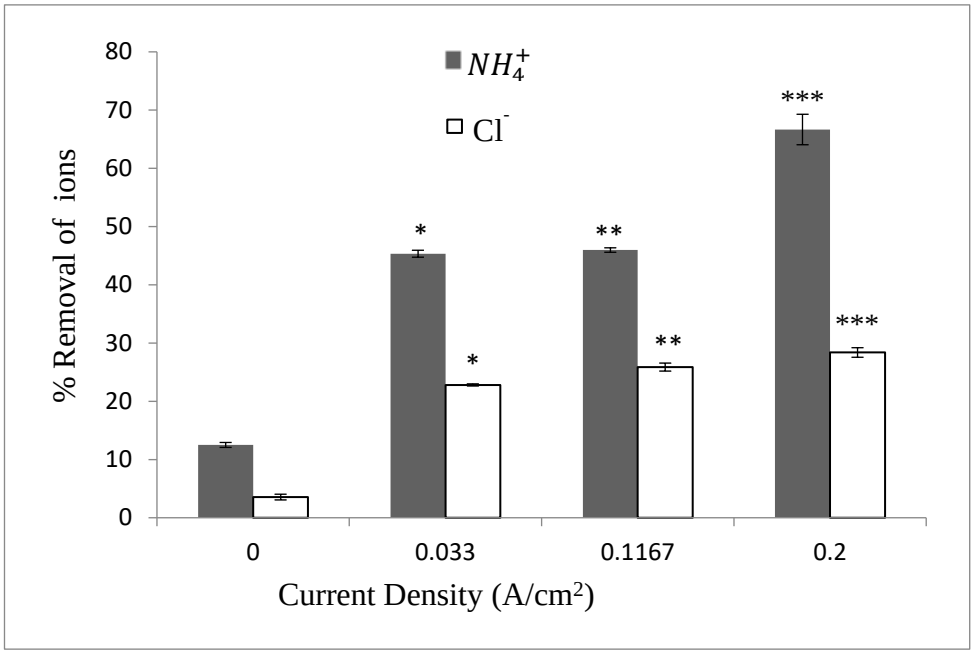

Figure 3.5: Effect of current density on the percentage removal of NH_4^+ and Cl^- ions after 6 hours at 20°C and initial concentrations of 14250 mg/l and 20000 mg/l of NH_4^+ and Cl^-, respectively. * Comparison between the percentage removals at 0 and 0.033 A/cm^2 (p-value = 0.00024 and 0.00037 for NH_4^+ and Cl^- respectively). **Comparison between the percentage removals at 0.033 and 0.1167 A/cm^2 (p-value = 0.336 and 0.0255 for NH_4^+ and Cl^- respectively). *** Comparison between the percentage removals at 0.1167 and 0.2 A/cm^2 (p-value = 0.008 and 0.0805 for NH_4^+ and Cl^- respectively)

As shown in Figures 3.5, when no current was applied a very small removal percentage of 12.5% and 3.55% for ammonium and chloride, respectively. Increasing the current density from 0 to 0.033 A/cm^2 show a significant effect on the removal of both ions NH_4^+ and Cl^-, where the removal percentage were 45.33% (p-value = 0.00024) and 22.8% (p-value = 0.00037), respectively. This suggests that the removal was mainly due to electrocoagulation. And the removal due to evaporation is minimal in comparison to the removal due to electrocoagulation. The increase in current density by 0.083 A/cm^2 to 0.1167 A/cm^2 did not show a significant effect on the removal of NH_4^+, where the removal increased only to 45.96% (p-value = 0.336). However, it was significant for Cl^- where the removal increased to 25.8% (p-value =

0.0255). The increase in the current density by 0.083 A/cm^2 to 0.2 A/cm^2 resulted in a significant effect on NH_4^+ removal of 66.66% (p-values = 0.008), but was in significant for Cl$^-$ with a removal of 28.37% (p-value = 0.0805).

The effect of current density in the range of 0 to 0.2 A/cm^2, on the rate of removal of NH_4^+ and Cl$^-$ ions was also tested at 20°C and at initial concentration of 14250 mg/l and 20000 mg/l of NH_4^+ and Cl$^-$, respectively, The experiment was done, and the data was found in appendix (A). This was used to determine the percentage removal shown in Figure 3.6.

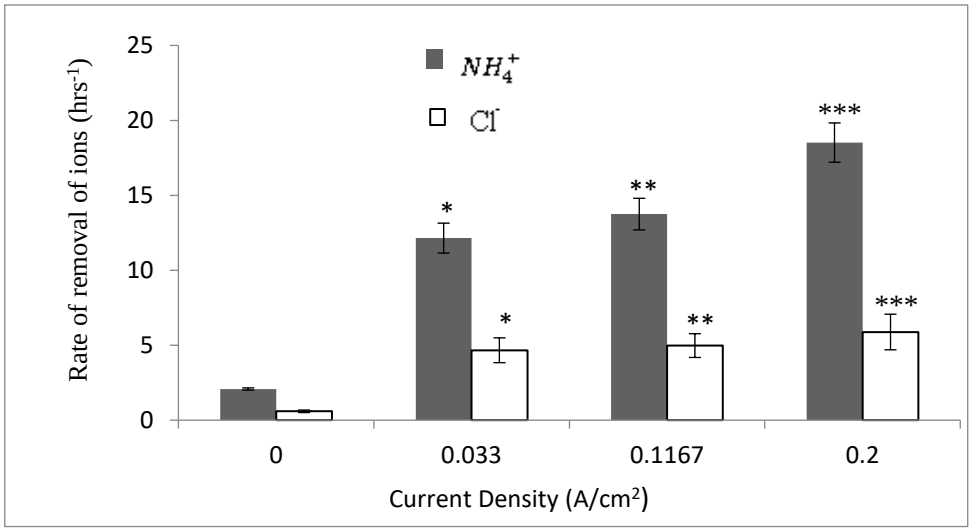

Figure 3.6: Effect of current density on the rate of removal of NH_4^+ and Cl$^-$ ions at 20°C and initial concentrations of 14250 mg/l and 20000 mg/l of NH_4^+ and Cl$^-$, respectively. * Comparison between the percentage removals at 0 and 0.033 A/cm^2 (p-value = 0.0049 and 0.02 for NH_4^+ and Cl$^-$ respectively). **Comparison between the rate of removals at 0.033 and 0.1167 A/cm^2 (p-value = 0.259 and 0.735 for NH_4^+ and Cl$^-$ respectively). *** Comparison between the rate of removals at 0.1167 and 0.2 A/cm^2 (p-value = 0.056 and 0.464 for NH_4^+ and Cl$^-$ respectively)

The results in Figure 3.6 show that the rate of removal of both ions, NH_4^+ and Cl$^-$, increased with the increase in current density. When no current was applied, a very small removal rates of NH_4^+ and Cl$^-$ was recorded, which were 2.08 hr^{-1} and 0.59 hr^{-1}, respectively. The increase in current density from 0 to 0.033 A/cm^2 showed a

significant effect on the rate of removal of both ions NH_4^+ and Cl^-, with rate of removal of 12.1 hr^{-1} (p-value = 0.0049) and 4.66 hr^{-1} (p-value 0.02) respectively. The increase in current density by 0.083 A/cm^2 to 0.1167 A/cm^2 did not show a significant effect on the rate of removal of NH_4^+ and Cl^-, with rate of removals increasing to 13.7 hr^{-1} (p-value = 0.259) and 4.97 hr^{-1} (p-value = 0.735), respectively. The increase in by another 0.083 A/cm^2 to 0.2 A/cm^2 also resulted in a minimal effect on NH_4^+ and Cl^- rate of removal, with the rate of removal increased to 18.5 hr^{-1} (p-value = 0.056) and 5.88 hr^{-1} (p-value = 0.464), respectively.

For the effect of the current density, it was found that as the value of current density increased, the residual ions concentration and the rate decreased. This is mainly due to the increase in the charge loading with increase in the current density. In addition, a better separation can be obtained by electro flotation by smaller bubbles generated during electrocoagulation (Sasane & Korke, 2015). Increases in current density, causes an increase in the amount of hydrogen bubbles which evolved at the cathode and as a result of that greater upwards flux and a faster removal of the pollutant and sludge flotation takes place. The results in this work agree those found for the removal of hexavalent chromium from wastewater by electrocoagulation (El-Taweel et al., 2015). However, the initial concentrations tested were in the range of 40-200 mg/l, which were much lower than the ones tested in this work. In addition, the current density tested was in the range from 0.0005 to 0.002 A/cm^2, which was also lower than the range used in this work (El-Taweel et al., 2015). The result agrees with previous experimental work done using electrocoagulation in a waste water contains a synthetic ammonia and different sodium chloride concentration and in the range of 0.005 A/cm^2 to 0.05 A/cm^2. It was also shows that at lower current density,

hypochlorite acid was produced in a less amount which was not enough to oxidize most of the ammonia (Can et al., 2014).

3.2 Effect of the Initial Concentration

The effect of initial concentration on the percentage removal of NH_4^+ and Cl^-, at 20°C and at current density of 0.1167 A/cm^2 was assessed by changing the percentage dilution of solutions with the maximum concentrations of NH_4^+ and Cl^-.

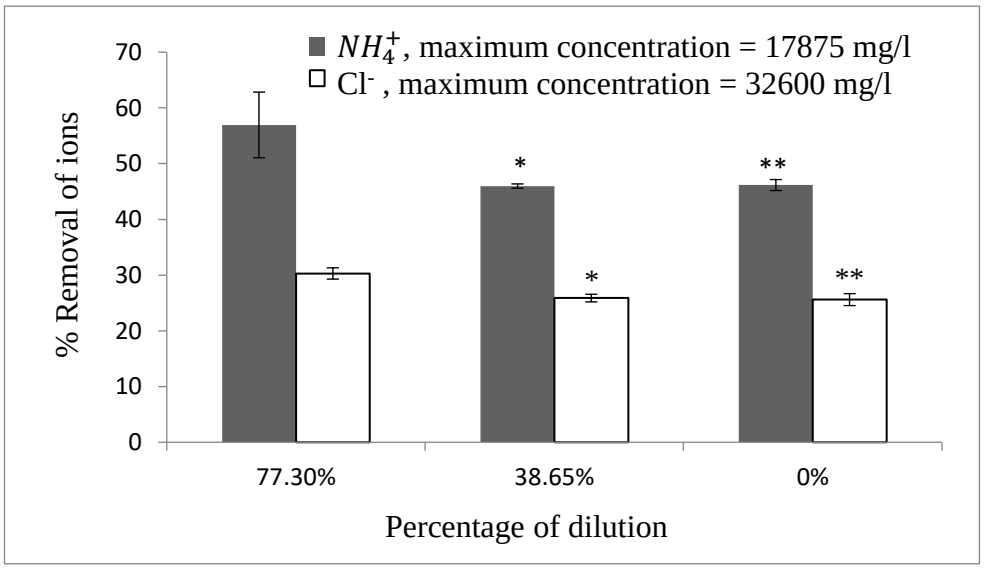

Figure 3.7: Effect of initial concentration of NH_4^+ and Cl^- on the percentage removal of the ions at 20°C and 0.1167 A/cm^2.*Comparison between percentage dilutions of 77.3% and 38.65% (p-value = 0.119 and 0.036 for NH_4^+ and Cl^- respectively). ** Comparison between percentage dilutions of 38.65% and 0% (p-value = 0.826 and 0.787 for NH_4^+ and Cl^- respectively)

The results in Figure 3.7 show that the percentage removal of both ions, NH_4^+ and Cl^- decreased with the decreases in the percentage dilution of the maximum concentration of NH_4^+ and Cl^-. The decreases from 77.3% to 38.65% causes a decrease in the percentage of removal from 56.9% to 45.9% with (p-value = 0.119) and from 30.2% to 25.8% with (p-value = 0.036) for NH_4^+ and Cl^-, respectively.

Further decrease in the percentage of dilution from 38.65% to 0% of NH_4^+ and Cl^- shows a decrease in the percentage of removal from 45.9% to 45.2% with (p-value = 0.826) and from 25.8% to 25.5% with (p-value = 0.787) for NH_4^+ and Cl^-, respectively.

The effect of initial concentration on the percentage rate of removal of NH_4^+ and Cl^-, at 20°C and at current density of 0.1167 A/cm^2 was assessed by changing the percentage dilution of solutions with the maximum concentrations of NH_4^+ and Cl^-.

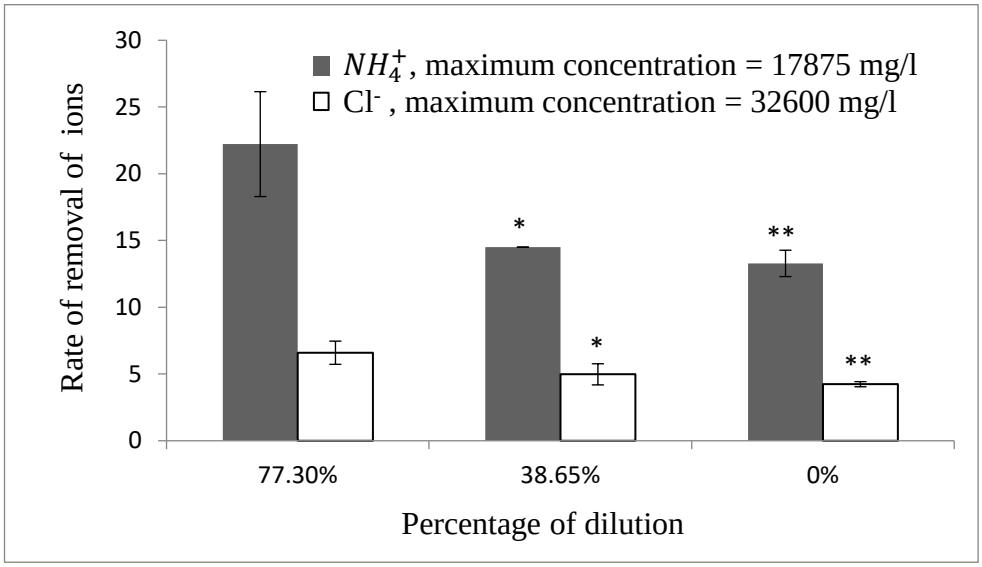

Figure 3.8: Effect of initial concentration of NH_4^+ and Cl^- on the rate of removal of the ions at 20°C and 0.1167 A/cm^2. *Comparison between percentage dilutions of 77.3% and 38.65% (p-value = 0.108 and 0.191 for NH_4^+ and Cl^- respectively). ** Comparison between percentage dilutions of 38.65% and 0% of the maximum concentration of NH_4^+ and Cl^- (p-value = 0.225 and 0.328 for NH_4^+ and Cl^- respectively)

The results in Figure 3.8 show that the rate of removal of both ions, NH_4^+ and Cl^- decreased with the decreases in the percentage dilution of the maximum concentration of NH_4^+ and Cl^-. The decreases from 77.3% to 38.65% causes a decrease in the rate of removal from 22.2 hr^{-1} to 14.4 hr^{-1} with (p-value = 0.108) and from 6.5 hr^{-1} to 4.9 hr^{-1} with (p-value = 0.191) for NH_4^+ and Cl^-, respectively. Further

decrease in the percentage of dilution from 38.65% to 0% of NH_4^+ and Cl^- shows a decrease in the rate of removal from 14.4 hr^{-1} to 13.28 hr^{-1} with (p-value = 0.225) and from 4.9 hr^{-1} to 4.2 hr^{-1} with (p-value = 0.328) for NH_4^+ and Cl^-, respectively.

For the effect of the initial concentration, it was found that as the value of initial concentration increased, both the percentage and rate of removal of NH_4^+ and Cl^- ions decreased and the pH decreases slightly with time. At the same current density, the same amount of Fe^{3+} passed through the solution for all concentration, and as a result the amount of Fe^{3+} released was insufficient at the higher concentration (Can et al., 2014). Also, the amount of the formed metal hydroxide flocs may not be enough to settle the huge amount of the pollutant molecules at the higher initial concentrations (Naje et al., 2016). The result agrees with previous experimental work done for the removal of nutrients from waste water, however, the tested concentrations and current densities were much lower than those tested in this work. The experiments were done at 0.0008 A/cm^2 which is also lower than the current density in this work where the minimum current density used in this work was 0.033 A/cm^2. It was also found that increasing the initial nutrient concentrations resulted in lower removal where the ammonium, removals was decreased from 93% to 75% and the phosphorous removal decreased from 76% to 45% (Tian et al., 2016) where in this work increases the initial concentration of ammonium from 4500 to 17875 mg/l decreases the percentage of removal from 56.9% to 45.27%. Another study was done to evaluate the effect of the initial arsenic concentration (10 – 100 mg/l) on the removal of the arsenic contamination in the drinking water by electrocoagulation using iron electrodes at pH 4, current density 0.54 mA/cm^2 and the electrolysis time of 30 minutes, also showed that increasing the initial arsenic

concentration decreased arsenic removal. Another experiment was done to investigate the enhanced removal of methylene blue by electrocoagulation using iron electrodes. Different initial concentration ranging from 25-100 mg/l were treated by EC, at 8 mA/cm^2 and 25°C and it was also found that increasing the initial concentration from 25-100 mg/l lead to decrease the percentage of removal of Methylene Blue from 99% to 90% (Mahmoud et al., 2013).

3.3 Effect of the Temperature

The effect of temperature, in the range of 3.2 to 36.8°C, on the percentage removal of NH_4^+ and Cl$^-$ ions was tested at initial concentration of 14250 mg/l and 20000 mg/l of NH_4^+, and Cl$^-$ respectively, and 0.1167 A/cm^2.

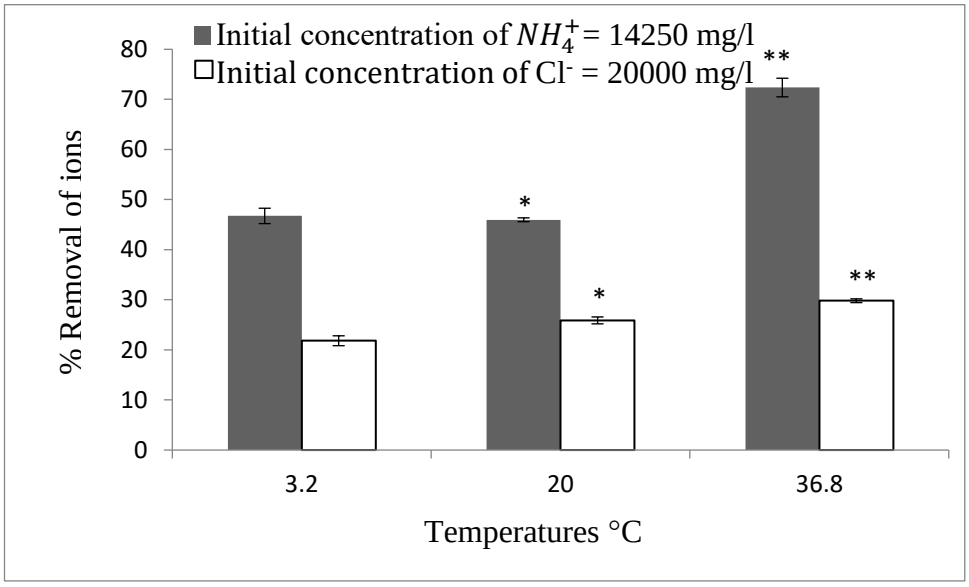

Figure 3.9: Effect of temperature on percentage removal of NH_4^+, and Cl$^-$ ions after 6 hours at 0.1167 A/cm^2 and initial concentrations of 14250 mg/l and 20000 mg/l of NH_4^+, and Cl$^-$ ions. * Comparison between different temperatures of 3.2°C and 20°C (p-value = 0.561 and 0.0409 for NH_4^+ and Cl$^-$ respectively). ** Comparison between different temperatures of 20°C and 36.8°C (p-Value = 0.00257 and 0.0192 for NH_4^+ and Cl$^-$ respectively)

The results in Figure 3.9 show that the percentage of removal of both ions, NH_4^+ and Cl^-, increased with the increase in temperature. The increases in temperature from 3.2 to 20°C increase the percentage of removal from 42.9% to 45.9% and from 21.8% to 25.8% with (p-value = 0.38 and 0.04 for NH_4^+ and Cl^-, respectively. However, increases in the temperature from 20 to 36.8°C resulted in a significant increase in the removal on both ions from 45.9% to 72.3% and from 25.8% to 29.8% with p-value = 0.002 and 0.019 for NH_4^+ and Cl^-, respectively.

The effect of temperature, in the range of 3.2 to 36.8°C on the rate of removal of NH_4^+ and Cl^- ions was tested at initial concentration of 14250 mg/l and 20000 mg/l of NH_4^+, and Cl^- respectively, and 0.1167 A/cm^2.

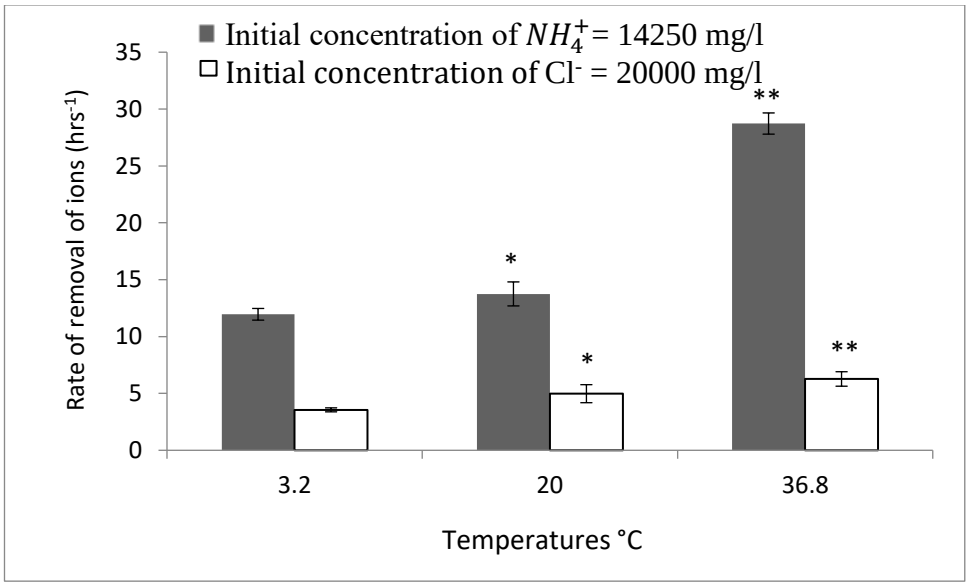

Figure 3.10: Effect of temperature on rate of removal of NH_4^+, and Cl^- ions at 0.1167 A/cm^2 and initial concentrations of 14250 mg/l and 20000 mg/l of NH_4^+, and Cl^- ions. * Comparison between different temperatures of 3.2°C and 20°C (p-value = 0.163 and 0.131 for NH_4^+ and Cl^- respectively). ** Comparison between different temperatures of 20°C and 36.8°C (p-Value = 0.00438 and 0.213 for NH_4^+ and Cl^- respectively)

The results in Figure 3.10 show that the rate of removal of both ions, NH_4^+ and Cl^-, increased with the increase in temperature. The increases in temperature from 3.2 to 20°C increase the rate of removal from 11.9 hr^{-1} to 13.7 hr^{-1} and from 3.5 hr^{-1} to 4.9 hr^{-1} with (p-value = 0.163 and 0.131 for NH_4^+ and Cl^-, respectively. However, increases in the temperature from 20 to 36.8°C resulted in a significant increase in the rate of removal of NH_4^+ where it increases from 13.7 hr^{-1} to 28.7 hr^{-1}. But, it was not significant for the Cl^- removal, where it increased from 4.9 hr^{-1} to 6.2 hr^{-1} with p-value = 0.004 and 0.213 for NH_4^+ and Cl^-, respectively.

To evaluate the influence of temperature and initial concentration on the significance of the effect of current density on the percentage removal of the ions, the experiment was repeated at different temperatures (10 and 30°C) and different initial concentrations (10437.5 and 15593.75 mg/L for NH_4^+ and 12500 and 27500 mg/L of Cl^-). The results for NH_4^+ and Cl^- are shown in Figures 3.11 and 3.12 respectively.

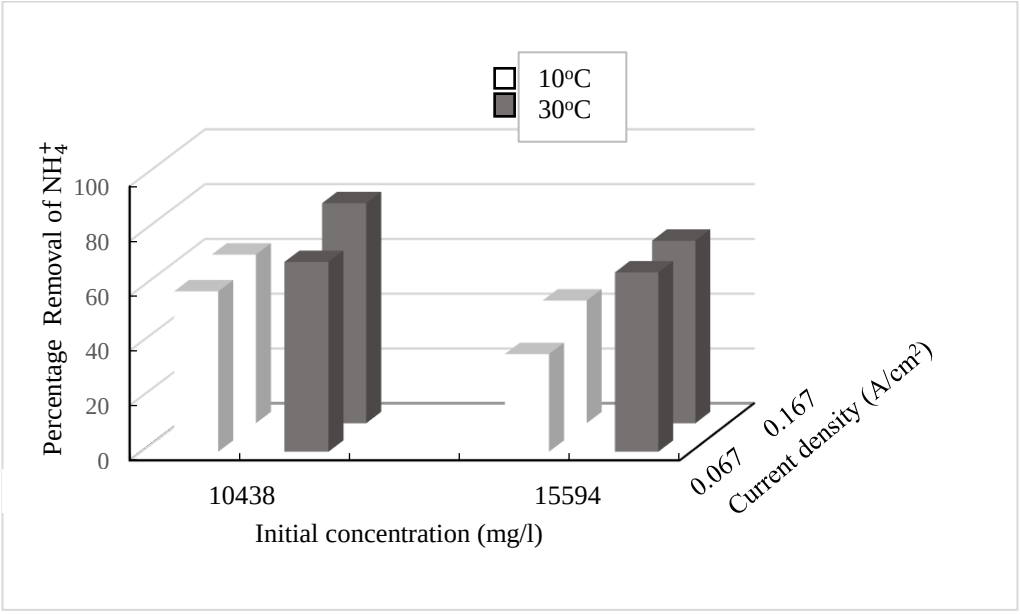

Figure 3.11: Effect of current density and initial concentration on the percentage of removal of NH_4^+ ion after 6 hours at 10°C and 30°C

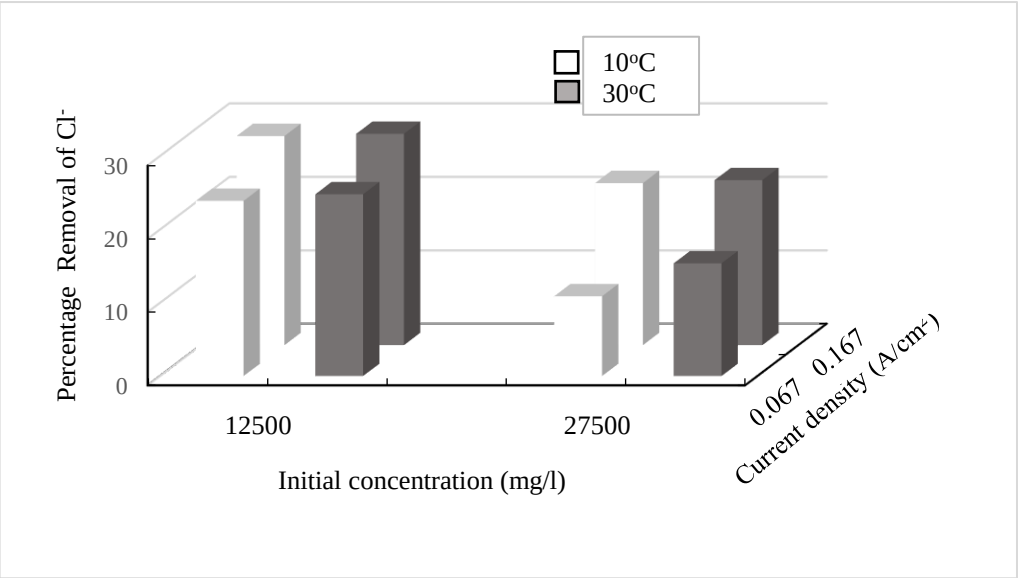

Figure 3.12: Effect of current density and initial concentration on the percentage of removal of Cl^- ion after 6 hours at 10°C and 30°C

As shown in Figures 3.11 and 3.12, the increase in initial concentration reduced the overall removal but increased the significance of the current density. On the other hand, at the lower initial concentrations, increasing the temperature from 10 to 30°C increased the percentage of removal and the significance of the current density effect of both ions. At 10°C, as the current density increased from 0.067 to 0.167 A/cm^2 the removal increased from 58.5% to 61.5% (p-value = 0.218) and from 23.9% to 28.5% (p-value = 0. 0.015) for NH_4^+ and Cl^-, respectively, and at 30°C the removal increases from 69.2% to 80.05% (p-value = 0.0015) and from 24.8% to 28.7% (p-value = 0.001) for NH_4^+ and Cl^-, respectively. At the higher initial concentration, increasing the temperature from 10 to 30°C increased the percentage of removal, however it lower the significance of the current density effect of NH_4^+ and Cl^-, where at 10°C the removal increases from 35.6% to 44.7% (p-value = 0.025) and from 10.9% to 22.1% (p-value = 0.093) for NH_4^+ and Cl^- respectively, and at 30°C the removal increases from 65.4% to 66.6% (p-value = 0.121) and from 15.4%

to 22.4% (p-value = 0.094) for NH_4^+ and Cl^- respectively. But for the initial concentration effect, the results shown in Figures 3.11 and 3.12 also show decrease in the removal with increase in initial concentration. In general, the increases in temperature increased the significance of the initial concentration. At the lower temperature, increasing the initial concentration from 10437.5 to 15593.75 mg/l, results in a decrease in the percentage of removal of NH_4^+ from 58.5% to 35.65% with (p-value = 0.006) and from 61.5% to 44.7% with (p-value = 0.0051), at the current density of 0.067 A/cm^2 and 0.167 A/cm^2, respectively. Likewise, for the chloride, increasing the initial concentration from 12500 to 27500 mg/l, results in a decrease in the percentage of removal of Cl^- from 23.9% to 10.9% with (p-value = 0.073) and from 28.5% to 22.1% with (p-value = 0.0036). At the higher temperature, increasing the initial concentration from 10437.5 to 15593.75 mg/l, results in a decrease in the percentage of removal of NH_4^+ from 69.25% to 65.04% with (p-value = 0.006) and from 80.3% to 66.6% with (p-value = 0.0016), at the current density of 0.067 A/cm^2 and 0.167 A/cm^2, respectively. For the chloride, increasing the initial concentration from 12500 to 27500 mg/l, results in a decrease in the percentage of removal of Cl^- from 24.8% to 15.4% with (p-value = 0.05) and from 28.7% to 22.4% with (p-value = 0.007). On the other hand, for the effect of the temperature, the results shown in Figures 3.11 and 3.12 also show an increase in the removal with the increase in temperature. At the lower current density, and initial concentration of 10437.5 mg/l and 12500 mg/l of NH_4^+ and Cl^-, respectively, increasing the temperature from 10 to 30°C lead to increase in the percentage of removal from 58.5% to 69.2% and from 23.9% to 24.8% with p-value = 0.25 and 0.26 of NH_4^+ and Cl^-, respectively. Increasing the initial concentration to 15593.75 mg/l and 27500 mg/l of NH_4^+ and Cl^-, respectively causes an increase in the percentage of removal

from 35.6% to 65.4% (p-value = 0.001) and from 10.9% to 15.44% (p-value = 0.41) of NH_4^+ and Cl^-, respectively. At initial concentration of 10437.5 mg/l and 12500 mg/l of NH_4^+ and Cl^-, respectively, increasing the temperature from 10 to 30°C lead to increase in the percentage of removal from 61.5% to 80% and from 28.5% to 28.7% with p-value = 0.0002 and 0.104 of NH_4^+ and Cl^-, respectively. Increasing the initial concentration as well as the higher current density, lead to decrease the significance of the removal of NH_4^+ and Cl^-, where at the higher current density, and at initial concentration of 15593.75 mg/l and 27500 mg/l of NH_4^+ and Cl^-, respectively, causes an increase in the percentage of removal from 22.1% to 22.4% with p-value = 0.003 and 0.66 of NH_4^+ and Cl^-, respectively.

The performance of the current density might be affected by the temperature and the initial concentration of the solution. To evaluate the effect of temperature and initial concentration on the significance of the effect of current density on the rate of removal of the ions, the experiment was repeated at different temperatures (10 and 30°C) and different initial concentrations (10437.5 and 15593.75 mg/L for NH_4^+) and (12500 and 27500 mg/L of Cl^-). Also, the performance of the initial concentration might be affected by the temperature and the current density. To evaluate the effect of temperature and current density on the significance of the effect of initial concentration on the rate of removal of the ions, the experiment was repeated at different current densities (0.067 and 0.167 A/cm^2) and different temperatures (10 and 30°C). In addition to that, the performance of the temperature might be affected by the initial concentration of the solution and the current density. To evaluate the effect initial concentration and current density on the significance of the effect of temperature on the rate of removal of the ions, the experiment was repeated at

different current densities (0.067 and 0.167 A/cm^2) and different initial concentration (10437.5 and 15593.75 mg/l of NH_4^+) and (12500 and 27500 mg/l of Cl$^-$). The results for NH_4^+ and Cl$^-$ are shown in Figures 3.13 and 3.14 respectively.

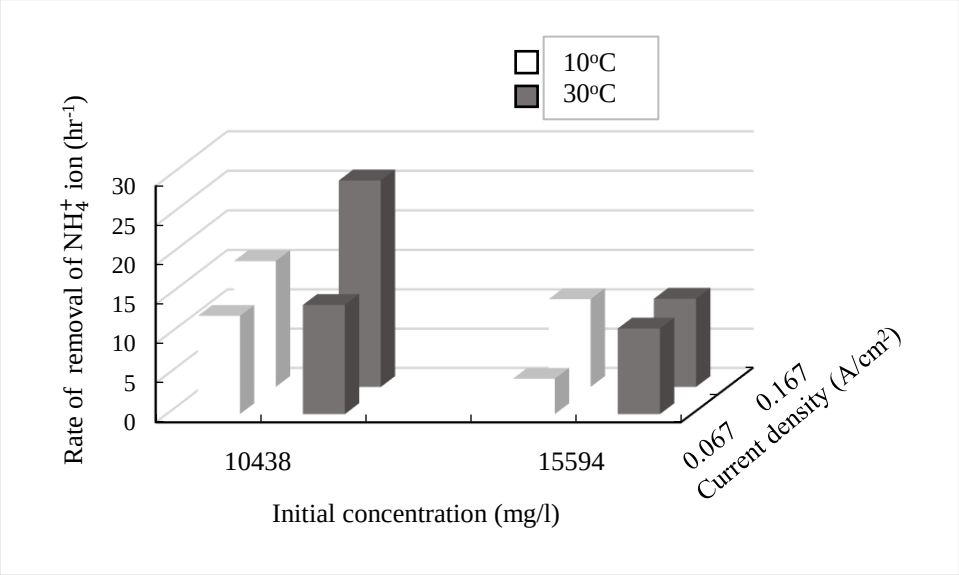

Figure 3.13: Effect of current density and initial concentration on the rate of removal of NH_4^+ ion at 10°C and 30°C

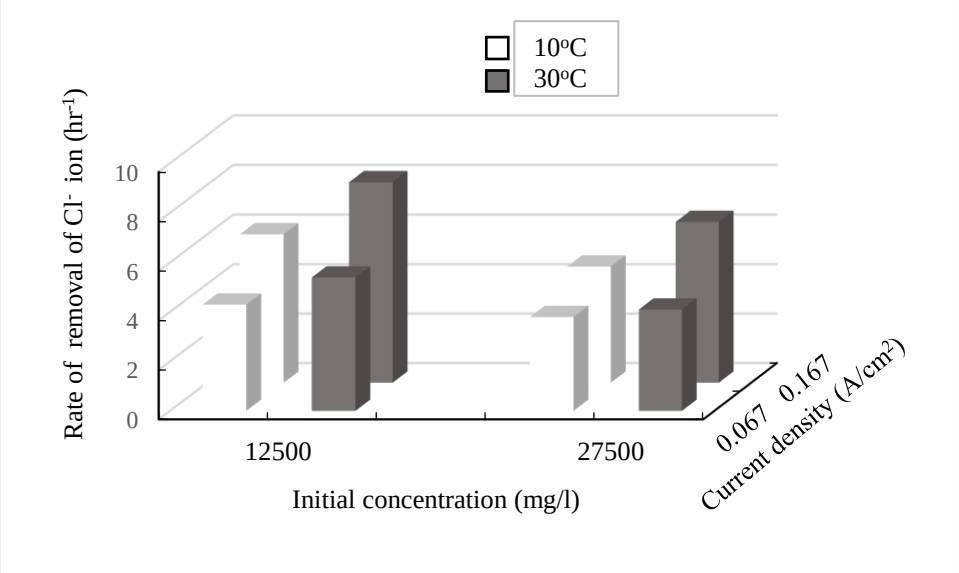

Figure 3.14: Effect of current density and initial concentration on the rate of removal of Cl$^-$ ion at 10°C and 30°C

For the current density, the results shown in Figures 3.13 and 3.14 also display an increase in the rate of removal with the increase in current density. At the lower initial concentration, increasing the temperature from 10 to 30°C increased the percentage rate of removal and the significance of the current density effect of NH_4^+ and Cl^-, where at 10°C the percentage rate of removal increases from 12.5 hr^{-1} to 16 hr^{-1} (p-value = 0.087) and from 4.2 hr^{-1} to 6 hr^{-1} (p-value = 0.13) for NH_4^+ and Cl^- respectively, and at 30°C the percentage rate of removal increases from 13.8 hr^{-1} to 26.2 hr^{-1} (p-value = 0.003) and from 5.3 hr^{-1} to 8 hr^{-1} (p-value = 0.055) for NH_4^+ and Cl^- respectively. However, at the higher initial concentration, increasing the temperature from 10 to 30°C increased the percentage rate of removal where at 10°C the percentage rate of removal increases from 4.4 hr^{-1} to 11.1 hr^{-1} (p-value = 0.051) and from 3.7 hr^{-1} to 4.6 hr^{-1} (p-value = 0. 39) for NH_4^+ and Cl^- respectively, and at 30°C the percentage rate of removal increases from 10.9 hr^{-1} to 11.22 hr^{-1} (p-value = 0.503) and from 4 hr^{-1} to 6.4 hr^{-1} (p-value = 0.04) for NH_4^+ and Cl^- respectively. For the initial concentration, the results shown in Figures 3.13 and 3.14 also show decrease in the removal with increase in initial concentration. In general, the increases in temperature increased the significance of the initial concentration. At the lower temperature, increasing the initial concentration from 10437.5 to 15593.75 mg/l, results in a decrease in the percentage of removal of NH_4^+ from 12.5 hr^{-1} to 4.4 hr^{-1} with (p-value = 0.03) and from 16 hr^{-1} to 11.1 hr^{-1} with (p-value = 0.067), at the current density of 0.067 A/cm^2 and 0.167 A/cm^2, respectively. Likewise, for the chloride, increasing the initial concentration from 12500 to 27500 mg/l, results in a decrease in the percentage of removal of Cl^- from 4.2 hr^{-1} to 3.7 hr^{-1} with (p-value = 0.632) and from 6 hr^{-1} to 4.6 hr^{-1} with (p-value = 0.17) at the current density of 0.067 A/cm^2 and 0.167 A/cm^2. At the higher temperature, increasing the initial

concentration from 10437.5 to 15593.75 mg/l, results in a decrease in the percentage rate of removal of NH_4^+ from 13.8 hr^{-1} to 10.9 hr^{-1} with (p-value = 0.05) and from 26.2 hr^{-1} to 11.2 hr^{-1} with (p-value = 0.00088), at the current density of 0.067 A/cm^2 and 0.167 A/cm^2, respectively. For the chloride, increasing the initial concentration from 12500 to 27500 mg/l, results in a decrease in the percentage rate of removal of Cl^- from 5.39 hr^{-1} to 4 hr^{-1} (p-value = 0.04) and from 8.08 hr^{-1} to 6.4 hr^{-1} (p-value = 0.171). And finally, for the temperature, the results shown in Figures 3.13 and 3.14 also show an increase in the rate of removal with the increase in temperature. At the lower current density, and initial concentration of 10437.5 mg/l and 12500 mg/l of NH_4^+ and Cl^-, respectively, increasing the temperature from 10 to 30°C lead to increase in the rate of removal from 12.5 hr^{-1} to 13.8 hr^{-1} (p-value = 0.265) and from 4.2 hr^{-1} to 5.3 hr^{-1} (p-value = 0.256). Increasing the initial concentration to 15593.75 mg/l and 27500 mg/l of NH_4^+ and Cl^-, respectively causes an increase in the rate of removal from 4.49 hr^{-1} to 10.9 hr^{-1} (p-value = 0.03) and from 3.7 hr^{-1} to 4.06 hr^{-1} (p-value = 0.673), respectively. At initial concentration of 10437.5 mg/l and 12500 mg/l of NH_4^+ and Cl^-, respectively, increasing the temperature from 10 to 30°C lead to increase in the rate of removal from 16 hr^{-1} to 26.2 hr^{-1} (p-value = 0.0099) and from 6 hr^{-1} to 8 hr^{-1} (p-value = 0.088), respectively. Increasing the initial concentration as well as the higher current density, lead to decrease the significance of the rate of removal of NH_4^+ and Cl^-, where at the higher current density, and at initial concentration of 15593.75 mg/l and 27500 mg/l of NH_4^+ and Cl^-, respectively, causes an increase in the rate of removal from 11.18 hr^{-1} to 11.2 hr^{-1} (p-value = 0.97) and from 4.6 hr^{-1} to 6.4 hr^{-1} (p-value = 0.114), respectively.

For the effect of the temperature, it was found that as the temperature value increased, the percentage and the rate of removal of NH_4^+ and Cl^- ions increased. This is due to the rate of diffusion of the ions which could increase with increasing the temperature of the solution (Wang et al., 2012). Also, the increase in the removal is obtained because when the temperature increases the mass transfer increases and the kinetic particles collision improved. Another reason for the removal of the ions is that the high temperature causes a formation of the hydrogen particles bubbles which enhances the flotation speed and causes a reduction in the suspended particles (Naje et al., 2016). The results agree with experimental work done using electrocoagulation for the waste water which contains a synthetic ammonia and different sodium chloride concentration, at current density ranges from (0.005 A/cm^2 to 0.05 A/cm^2) and temperature was increased from 25.0°C to 40.3°C. As a result of increasing the temperature, the ammonia oxidation rate increased (Wang et al., 2012). Studies were done to investigate the effect of the temperature on the removal of indium ion using electrocoagulation. The effect of temperature on the indium ion removal efficiency was studied at 14.85, 24.85, 34.85, and 44.85°C which is in the same range of the temperature which were studied in our cases (9.85 - 29.85°C). As the time of electrolysis increased, comparable increases in the indium ion removal efficiency were observed for the different temperatures. After 50 min of electrolysis, it seen that the indium ion removal efficiency reached 80.9%, 90.4%, 92.7%, and 94.1% for temperatures of 14.85, 24.85, 308, and 44.85°C, respectively (Chou and Huang, 2009). Another study showed an increase in the boron removal by EC, when the temperature increases from 19.85–59.85°C, the percentage removal of the boron ions increases from 84% to 96%. Further study was done to investigate the effect of the temperature on the percentage of the phenol removal using a fixed bed aluminum

electrode where the percentage of the removal increases from 88% to 95% when the temperatures increases from 25 to 45 °C (Naje et al., 2016).

3.4 Statistical Analysis

Minitab 17.0 software was used for regression analysis of the experimental data and to find the coefficients of a regression equation. Twenty runs were carried out, each run was repeated twice, and the relationship between the experimental levels of each factor and the responses was expressed by a fitted polynomial equation, which was then used to optimize the three individual factors. The significance of the factors was evaluated using the p-value, and the lack-of-fit value of the model was determined from the analysis of the variance.

3.4.1 Percentage Removal of Ammonium

Table 3.1: Results of the Minitab analysis of the experimental results of ammonium removal

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	2518.8	503.76	13.79	0.000
Linear	3	1942.4	647.45	17.72	0.000
Current density	1	268.3	268.35	7.34	0.017
Temperature	1	1245.1	1245.05	34.08	0.000
Initial concentration	1	429.0	428.95	11.74	0.004
Square	2	579.9	289.97	7.94	0.005
Current density*Current density	1	276.9	276.88	7.58	0.016
Temperature*Temperature	1	353.2	353.21	9.67	0.008
Error	14	511.5	36.54		
Lack-of-Fit	9	374.1	41.57	1.51	0.338
Pure Error	5	137.4	27.47		
Total	19	3030.3			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
6.04450	83.12%	77.09%	57.65%

The results indicated that the effect of current density, temperature and initial concentration were all significant (P-value < 0.05). The lack-of-fit implies that the fit was significant (P-value > 0.05). Figure 3.15 shows the residual plots for percentage removal of ammonium.

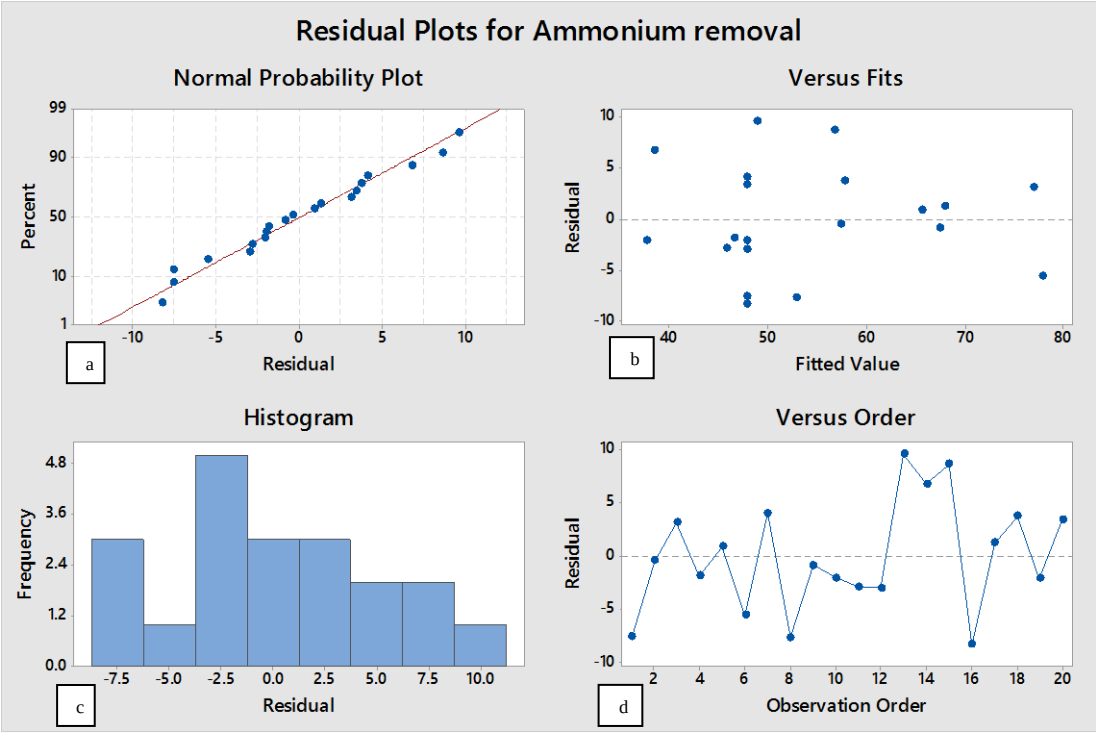

Figure 3.15: Residual plots for percentage removal of ammonium. a) Normal probability plot. b) Patterns in residuals versus fitted values plots to check the equal variance. c) Frequency verses the residual d) Residual verses the observation order to check the randomness

Figure 3.15-a shows verification of the assumption that the residuals are normally distributed, the normal plot of the residuals displays the difference between an observed value (blue points) and its corresponding fitted value (diagonal). The points in this plot should generally form a straight line along the diagonal if the residuals are normally distributed. If the points on the plot depart from a straight line, the normality assumption may be invalid. Figure 3.15-b shows verification of the assumption that the residuals have a constant variance, this plot should show a random pattern of residuals on both sides of 0. If a point lies far from the majority of

points, it may be an outlier. There should not be any recognizable patterns in the residual plot. For instance, if the spread of residual values tend to increase as the fitted values increase, then this may violate the constant variance assumption. Figure 3.15-c determine whether the data are skewed or whether outliers exist in the data, an exploratory tool to show general characteristics of the residuals including typical values, spread, and shape. A long tail on one side may indicate a skewed distribution. If one or two bars are far from the others, those points may be outliers. Figure 3.15-d shows verification of the assumption that the residuals are uncorrelated with each other; this plot helps you to check the assumption that the residuals are uncorrelated with each other.

After removing the insignificant factor, the predicted polynomial model of the ammonium removal, Y_1, as function of the significant factors and their combinations, was developed, as shown in Eq (14):

$$Y_1 = 77.3 - 324\ X_1 - 1.018\ X_2 - 0.000748\ X_3 + 1764\ X_1^2 + 0.493\ X_2^2 \qquad (14)$$

X_1, X_2 and X_3 are current density, temperature, and initial concentration

The developed polynomial was used to determine the effects of the three factors simultaneously in a 3-D surface response graphs shown in Figures 3.16-3.18:

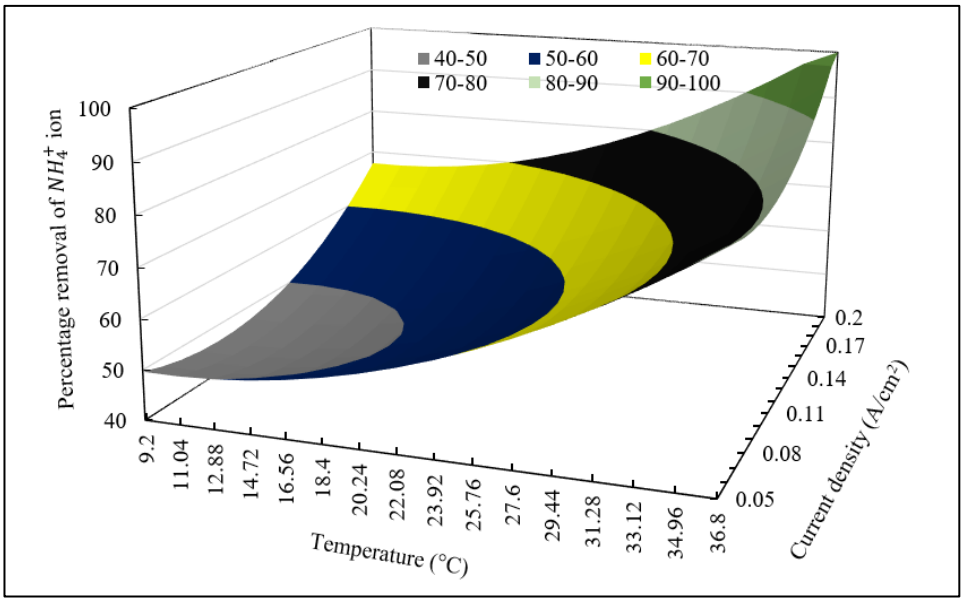

Figure 3.16: Effect of current density and temperature on the percentage removal of NH_4^+

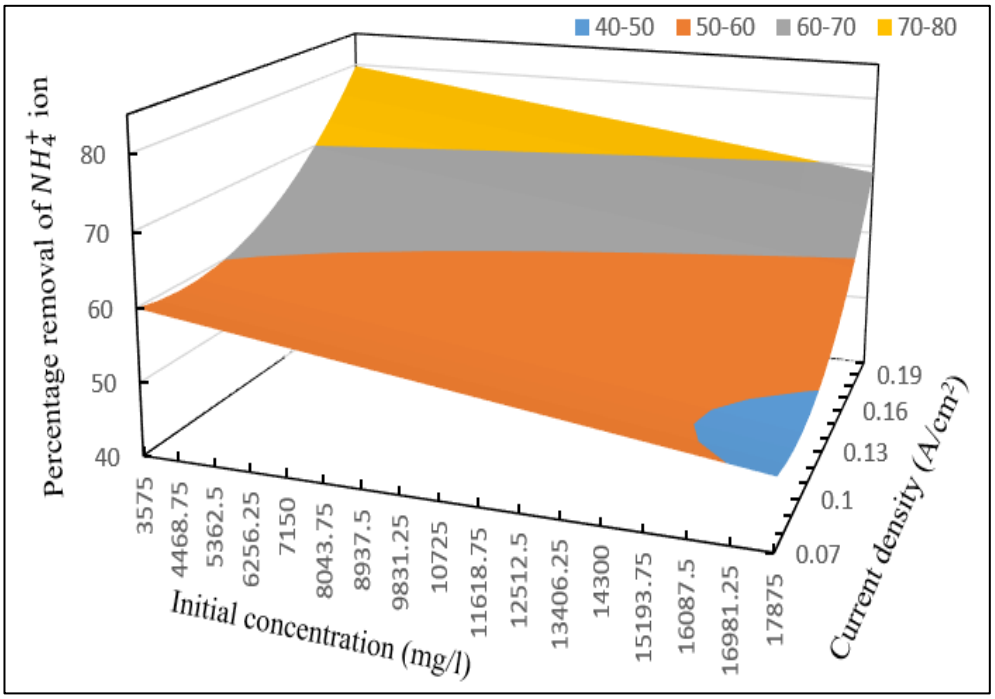

Figure 3.17: Effect of current density and initial concentration on the percentage removal of NH_4^+

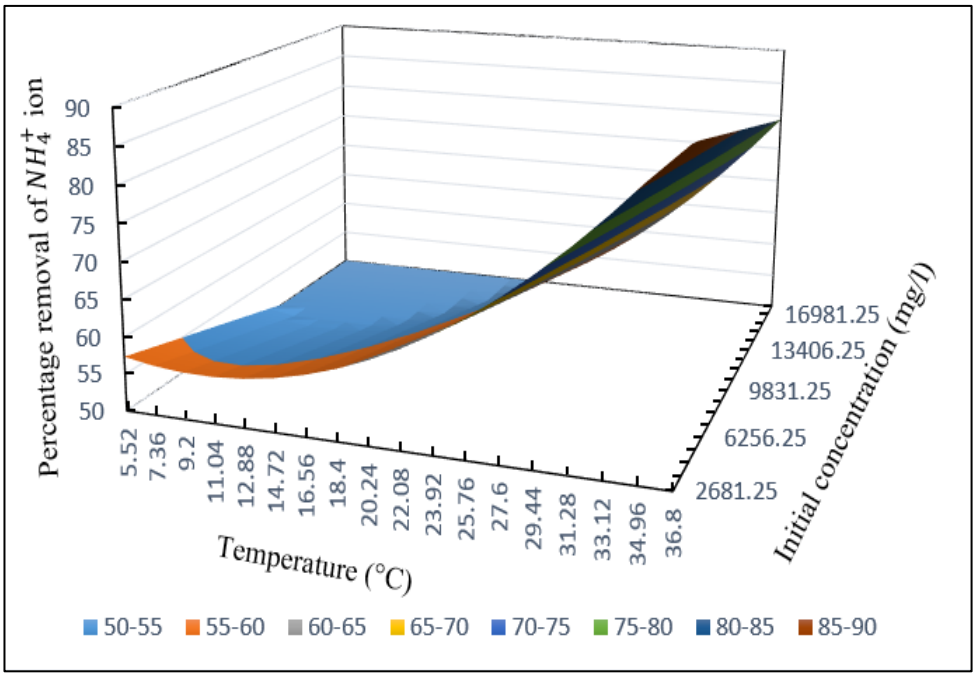

Figure 3.18: Effect of temperature and initial concentration on the percentage removal of NH_4^+

Figures 3.16-3.18 show that the percentage removal of NH_4^+ increased with increasing the temperature and current density, and decreasing the initial concentration.

3.4.2 Percentage Removal of Chloride

Similar tests to those done on ammonium and presented in Section 3.3.1.1. were applied to chloride removal and the results are shown in Table 3.2 and Figure 3.19. Table 3.2 shows the analysis of the variance, the effect of each factor (current density, and initial concentration) and their combinations, on the percentage of removal of chloride, and the lack of fit of the model.

Table 3.2: Results of the Minitab analysis of the experimental results of chloride removal

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	2	229.57	114.784	8.95	0.002
Linear	2	229.57	114.784	8.95	0.002
Current density	1	94.89	94.891	7.40	0.015
Initial concentration	1	134.68	134.677	10.50	0.005
Error	17	218.14	12.832		
Lack-of-Fit	12	187.22	15.602	2.52	0.158
Pure Error	5	30.91	6.183		
Total	19	447.71			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.58213	51.28%	45.54%	29.96%

The results indicated that the effect of current density and initial concentration were significant (P-value < 0.05). The lack-of-fit implies that the fit was significant (P-value > 0.05). Figure 3.19 shows the residual plots for percentage removal of chloride.

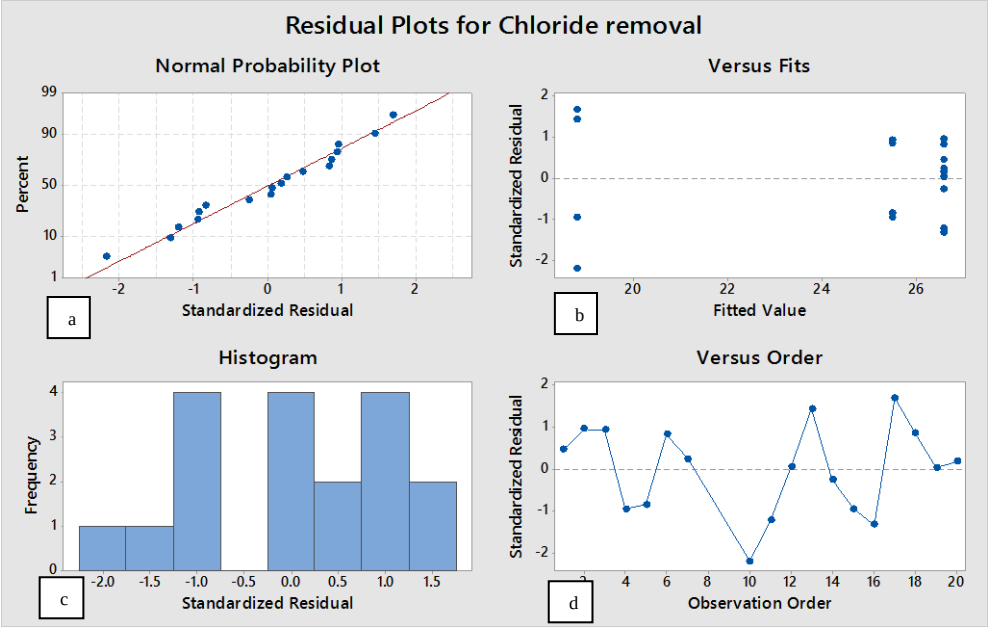

Figure 3.19: Residual plots for percentage removal of chloride. a) Normal probability plot. b) Patterns in residuals versus fitted values plots to check the equal variance. c) Frequency verses the residual d) Residual verses the observation order to check the randomness

Figure 3.19- a shows verification of the assumption that the residuals are normally distributed; the normal plot of the residuals displays the difference between an observed value (blue points) and its corresponding fitted value (diagonal). The points in this plot should generally form a straight line along the diagonal if the residuals are normally distributed. If the points on the plot depart from a straight line, the normality assumption may be invalid. Figure 3.19-b shows verification of the assumption that the residuals have a constant variance, this plot should show a random pattern of residuals on both sides of 0. If a point lies far from the majority of points, it may be an outlier. There should not be any recognizable patterns in the residual plot. For instance, if the spread of residual values tend to increase as the fitted values increase, then this may violate the constant variance assumption. Figure 3.19-c determine whether the data are skewed or whether outliers exist in the data, an

exploratory tool to show general characteristics of the residuals including typical values, spread, and shape. A long tail on one side may indicate a skewed distribution. If one or two bars are far from the others, those points may be outliers. Figure 3.19-d shows verification of the assumption that the residuals are uncorrelated with each other; this plot helps you to check the assumption that the residuals are uncorrelated with each other.

After removing the insignificant factor, the predicted model of the chloride removal, Y_2, as function of the significant factors and their combinations, was developed, as shown in Eq (15):

$$Y_2 = 26.90 + 52.9\ X_1 - 0.000419\ X_3 \qquad (15)$$

X_1 and X_3 are current density and initial concentration

The developed model was used to determine the effects of the two factors simultaneously in a 3-D surface response graphs shown in Figure 3.20:

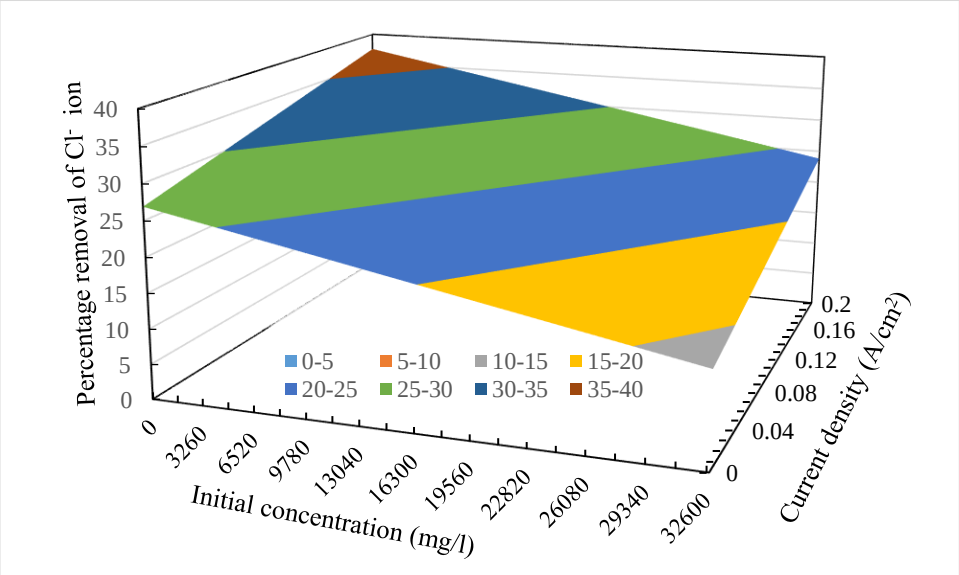

Figure 3.20: Effect of current density and the initial concentration on the percentage removal of Cl^-

Figure 3.20 shows that the percentage removal of Cl^- decreased with increasing the initial concentration and increased with increasing the current density.

3.4.3 Ammonium and Chloride Removal Optimization

An optimization process was implemented using response optimizer in Minitab, and the results are shown in Figure 3.21.

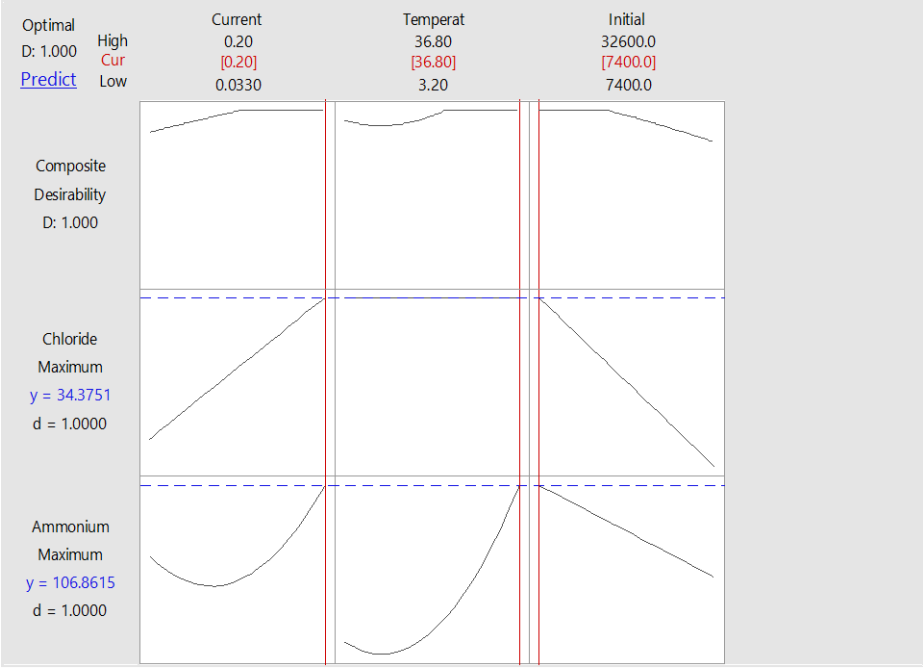

Figure 3.21: The optimization results of the effects of current density, temperature and initial concentration for maximum chloride and ammonium removals

Figure 3.21 shows that increasing the current density increased the removal of chloride linearly as only the individual effect was significant, wheareas the removal of ammonium was parabolic, due to the second order significant term. No effect of temperature was observed on the percentage of removal of chloride, as suggested by Eq (15), whereas, the percentage removal of ammonium increased parabolically. The initial concentration had a diverse effects on the percentage removals of ammonium

and chloride ions. The optimum removal for both ammonium and chloride ions was determined to be at a current density of 0.2 A/cm^2, temperature of 36.8°C and initial concentration of 7400 mg/l of chloride. At this condition, the removal percentages of ammonium and chloride were found to be 106.86% and 34.37%, respectively. An independent experiment was done at 0.1167 A/cm^2, and an initial concentrations of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, and at 30°C. At this condition, the removals of ammonium and chloride were found to be 71.55% and 26.88%, respectively. It was interesting to compare the removal percentage of chloride ions based on the total initial concentration of the ion, and based on initial ammonium chloride concentration generated in the Solvay process, which was taken to be equal to the initial concentration of NH_4^+. At current density of 0.1167 A/cm^2, an initial concentration of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, and at 30°C, and based on the initial NH_4Cl, the percentage removal of chloride was found to be 37.7%, compared to 26.88% based on the initial concentration of Cl^-.

Chapter 4: Conclusion

The performance of electrocoagulation for the removal of NH_4^+ and Cl^- from the effluent Solvay process was evaluated. The effects of temperature in the range of 3.2 - 36.8°C, initial concentration of chloride in the range of 7400 - 32600 mg/l, and current density in the range of 0.033 - 0.2 A/cm^2 were assessed in a batch electrocoagulation cell. Since the temperature and the current density effect was increasing throughout the tested range, and the initial concentration of ammonium and chloride ions effect was decreasing throughout the tested range then the best performance is achieved at the highest temperature, highest current density and the lowest initial concentration based on the predicted model (Eqs. 14 and 15).

At all tested temperatures and initial concentrations, increasing the current density always resulted in increase in the removal. For example, at 20°C and an initial concentrations of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, it was found that, increasing the current density from 0 to 0.2 A/cm^2 resulted in increasing in the removal percentage from 12.5 to 66.7% and from 3.55 to 28.4% for NH_4^+ and Cl^-, respectively. However, the effect of current density was more significant for the removal of NH_4^+ and Cl^- at lower initial concentration and higher temperature. At all tested current density and initial concentrations, increasing the temperature always resulted in increase in the removal. For example, at 0.1167 A/cm^2 and an initial concentrations of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, it was found that, increasing the temperature from 3.2 to 36.8°C, resulted in increasing in the removal from 42.9 to 72.4% and from 21.8 to 29.8% for NH_4^+ and Cl^- , respectively. However, the effect of temperature was more significant for the removal of NH_4^+ at lower initial concentration and higher current density, but the effect of temperature was not significant for the removal of Cl^-. At all

tested current density and temperature, increasing the initial concentration always resulted in decrease in the removal. For example, at a current density of 0.1167 A/cm^2 and 20°C, increasing the initial concentration of chloride from 7400 to 32600mg/l resulted in decreasing in the removal from 56.9 to 45.3% and from 30.3 to 25.6% for NH_4^+ and Cl^-, respectively. However, the effect of initial concentration was more significant for the removal of NH_4^+ at higher temperature and current density, whereas for Cl^- the effect of initial concentration was more significant at the lower temperature and higher current density.

The experimental results were used to develop a model to predict the removal of ammonium and chloride. The model was validated against an independent experimental point not used in the development of the model equation (Eqs. 14 and 15). At current density of 0.1167 A/cm^2, an initial concentration of 14250 mg/l and 20000 mg/l for ammonium and chloride, respectively, and at 30°C the removals of ammonium and chloride were found to be 71.55% and 26.88%, respectively. At this condition, the removal percentages predicted by the model Eqs. (14) and (15) were found to be 62.38% and 26.15% For NH_4^+ and Cl^-, respectively. The difference between the experimental results and the model predictions are ± 14.6% and ± 2.7% NH_4^+ and Cl^-, respectively, which shows the adequacy of the model. This models (Eqs. 14 and 15) can be used for scaling up the experiments at higher temperature, current density and lower initial concentration.

4.1 Recommended Future Work

The following future studies are recommend based on the experimental results:

1. For the ammonium and chloride removal, carry out the numerical modeling at different operating conditions.
2. To evaluate the performance of EC at different operating conditions, expand the study into a pilot-scale.

References

Ahmad, N., & Baddour, R. E. (2014). A review of sources, effects, disposal methods, and regulations of brine into marine environments. *Ocean & Coastal Management*, *87*, 1–7. https://doi.org/10.1016/j.ocecoaman.2013.10.020

Anderson-Cook, C. M., Borror, C. M., & Montgomery, D. C. (2009). Response surface design evaluation and comparison. *Journal of Statistical Planning and Inference*, *139*(2), 629–641. https://doi.org/10.1016/j.jspi.2008.04.004

Asselin, M., Drogui, P., Brar, S. K., Benmoussa, H., & Blais, J. (2008). Organics removal in oily bilgewater by electrocoagulation process, J. Hazard. Mater. 151, 446–455.

Can, B., Boncukcuoglu, R., Yilmaz, A., & Fil, B. (2014). Effect of some operational parameters on the arsenic removal by electrocoagulation using iron electrodes.

Chamber, H. (2004). Norcure Chloride Extraction. Fosroc International Limited. Retrieved from http://www.fosroc.com/

Cheah, S. (2000). Desalination. Retrieved November 3, 2016, from http://student.mathisasport.org/srittgers/desalination.html

Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.*, *38*, 11–41.

Chou, W.-L., & Huang, Y.-H. (2009). Electrochemical removal of indium ions from aqueous solution using iron electrodes. *Journal of Hazardous Materials*, *172*(1), 46–53. https://doi.org/10.1016/j.jhazmat.2009.06.119

Chou, J. W., Wang, C., & Huang, K. (2009). Effect of operating parameters on indium (III) ion removal by iron electrocoagulation and evaluation of specific energy consumption, J. Hazard. Mater. 167, 467–474.

Cotruvo, J. A. (2005). Desalination Guidelines Development for Drinking Water: Background. *Nutrients in Drinking Water*, 13.

Dawoud, M. A. (2005). The role of desalination in augmentation of water supply in GCC countries. *Desalination*, *186*(1–3), 187–198. https://doi.org/10.1016/j.desal.2005.03.094

Dengil, l. A., Kulac, S., & Ozacar, M. (2009). Treatment of tannery liming drum wastewater by electrocoagulation, J. Hazard. Mater. 167, 940–946.

Dutton, Z. (2014, February). The Solvay Process. Retrieved February 11, 2017, from https://prezi.com/hnat3e7uyeml/the-solvay-process/

El-Naas, M. H., Al-Zuhair, S., Al-Lobaney, A., & Makhlouf, S. (2009). Assessment of electrocoagulation for the treatment of petroleum refinery wastewater, J. Environ. Manage. 91, 180–185.

El-Naas, M. H. (2011a). Reject brine management. *Desalination, Trends and Technologies, Croatia, InTech*, 237–252.

El-Naas, M. H. (2011b). Teaching water desalination through active learning. *Education for Chemical Engineers*, *6*(4), e97–e102. https://doi.org/10.1016/j.ece.2011.08.001

El-Naas, M. H., Al-Marzouqi, A. H., & Chaalal, O. (2010). A combined approach for the management of desalination reject brine and capture of CO2. *Desalination*, *251*(1–3), 70–74. https://doi.org/10.1016/j.desal.2009.09.141

El-Taweel, Y. A., Nassef, E. M., Elkheriany, I., & Sayed, D. (2015). Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode. *Egyptian Journal of Petroleum*, *24*(2), 183–192. https://doi.org/10.1016/j.ejpe.2015.05.011

Emamjomeh, M. ., & Sivakumar. (2009). Denitrification using a monopolar electrocoagulation/flotation (ECF) process, J. Environ. Manage. 91, 516–522.

Emamjomeh, M. M., & Sivakumar, M. (2009). Fluoride removal by a continuous flow electrocoagulation reactor. *J. Environ. Manage*, *90*, 1204–1212.

Engelhardt, T. L. (2010). Coagulation, Flocculation and Clarification of Drinking Water, 5.

Esfahani, B., Koupaei, M., & Ghasemi, S. (2014). Industrial waste water treatment by membrane systems, *2014 Vol. 4 (S1)*, 1168–1177/Esfahani et al.

Espinoza-Quinones, F. R., Fornari, M. M. T., Modenes, A. N., Palacio, S. M., da Silva, F. G., Szymanski, N., … Trigueros. (2009). Pollutant removal from tannery effluent by electrocoagulation, Chem. Eng. J. 151, 59–65.

Fry, A., & Martin, R. (2005, August). Facts and trends. Retrieved from http://www.unwater.org/downloads/Water_facts_and_trends.pdf

Gomes, J. A. G., Daida, P., Kesmez, M., Weir, M., Moreno, H., Parga, J. R., … Cocke, D. L. (2007). Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products, *139*, 220–231.

Ghosh, D., Solanki, H., & Purkait, M. K. (2008). Removal of Fe(II) from tap water by electrocoagulation technique, J. Hazard. Mater. 155, 135–143.

Ghernaout, D., Badis, A., Kellil, A., & Ghernaout, B. (2008). Application of electrocoagulation in Escherichia coli culture and two surface waters, Desalination 219, 118–125.

Hamdan, S. S. (2014). Evaluation of electrocoagulation for the removal of chromium (VI) from brackish ground water. United Arab Emirates University, UAE.

Hanafi, F., Assobhei, O., & Mountadar, M. (2010). Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater. 174, 807–812.

Hasson, D., Lumelsky, V., Greenberg, G., Pinhas, Y., & Semiat, R. (2008). Development of the electrochemical scale removal technique for desalination applications. *Desalination*, *230*, 329–342.

Hu, C. Y., Lo, S. L., & Kuan, W. H. (2003). Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res. 37, 4513–4523.

Ilhan, F., Kurt, U., Apaydin, O., & Gonullu, M. T. (2008). Treatment of leachate by electrocoagulation using aluminum and iron electrodes. *Journal of Hazardous Materials*, *154*(1–3), 381–389. https://doi.org/10.1016/j.jhazmat.2007.10.035

Isaka, M. (2012, March). Water Desalination Using Renewable Energy. International Renewable Energy Agency. Retrieved from http://www.irena.org/Publications

Jirsa, F. (1950). The Electrolysis of Aqueous Solutions of Ammonium Iodide. *J. Am. Chem. Soc.*, 2831–2834. https://doi.org/10.1021/ja01163a003

Khawaji, A. D., Kutubkhanah, I. K., & Wie, J.-M. (2008). Advances in seawater desalination technologies, *221*, 47–69.

Khuri, A. I. (2003). Current modeling and design issues in response surface methodology: GLMs and models with block effects, *22*, 209–229.

Kobya, M., Senturk, E., & Bayramoglu. (2006). Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater. 133, 172–176.

Koparal, A. S., Yildiz, Y. s., Keskinler, B., & Demircioglu. (2008). Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59, 175–182.

Kumar, L., & Singh, S. K. (2015). Removal of chloride from ground water by Bio adsorption. *International Journal of Advance Research*, *3*(5), 140–154.

Labanowski, J., Pallier, V., & Feuillade-Cathalifaud, G. (2010). Study of organic matter during coagulation and electrocoagulation processes: Application to a stabilized landfill leachate, *179*, 166–172.

Lacasa, E., Canizares, P., Saez, C., Fernandez, F. J., & Rodrigo. (2011). Removal of nitrates from groundwater by electrocoagulation, Chem. Eng. J. 171, 1012–1017.

Le Dirach, J., Nisan, S., & Poletiko, C. (2005). Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems. *Desalination*, *182*(1–3), 449–460. https://doi.org/10.1016/j.desal.2005.02.037

Li, X., Song, J., Guo, J., Wang, Z., & Feng, Q. (2011). Landfill leachate treatment using electrocoagulation. *Procedia Environmental Sciences*, *10*, 1159–1164. https://doi.org/10.1016/j.proenv.2011.09.185

Mahmoud, M., Farah, J., & Farrag, T. (2013). Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes, *22*, 211–216.

Mohammad, A. F. M. (2015a). Optimization of a combined approach for the treatment of desalination reject brine and capture of CO_2. Retrieved from http://scholarworks.uaeu.ac.ae/cgi/viewcontent.cgi?article=1019&context=all_theses

Mohammad, A. F. M. (2015b). Optimization of a combined approach for the treatment of desalination reject brine and capture of CO_2. Retrieved from http://scholarworks.uaeu.ac.ae/cgi/viewcontent.cgi?article=1019&context=all_theses

Mollah, M., Morkovsky, P., Gomes, J., Kesmez, M., Parga, J., & Cocke, D. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials*, *114*(1–3), 199–210. https://doi.org/10.1016/j.jhazmat.2004.08.009

Mollah, M. Y. A., Schennach, R., Parga, J. R., & Cocke, D. L. (2001). Electrocoagulation (EC)—science and applications. *Journal of Hazardous Materials*, *84*(1), 29–41.

Mook, W. T., Chakrabarti, M. H., Aroua, M. K., Khan, G. M. A., Ali, B. S., Islam, M. S., & Abu Hassan, M. A. (2012). Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: A review. *Desalination*. Retrieved from http://agris.fao.org/agris-search/search.do?recordID=US201500090583

Moussa, D. T., El-Naas, M. H., Nasser, M., & Al-Marri, M. J. (2016). A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. *Journal of Environmental Management*, *186*, 24–41. https://doi.org/10.1016/j.jenvman.2016.10.032

Naje, A. S., Chelliapan, S., Zakaria, Z., Ajeel, M. A., & Alaba, P. A. (2016). A review of electrocoagulation technology for the treatment of textile wastewater. *Reviews in Chemical Engineering*, *0*(0). https://doi.org/10.1515/revce-2016-0019

Nanseu-Njiki, C. P., Tchamango, S. R., Ngom, P. C., Darchen, A., & Ngameni, E. (2009). Mercury(II) removal from water by electrocoagulation using aluminium and iron electrodes, J. Hazard. Mater. 168, 1430–1436.

Palaniappan, M., United Nations Environment Programme, Division of Environmental Policy Implementation, & Pacifica Institute. (2010). *Clearing the waters: a focus on water quality solutions*. Nairobi, Kenya; [Oakland, CA: United Nations Environment Programme, Division of Environmental Policy Implementation ; [Pacific Institute. Retrieved from http://www.unep.org/PDF/Clearing_the_Waters.pdf

Pérez-González, A., Urtiaga, A. M., Ibáñez, R., & Ortiz, I. (2012). State of the art and review on the treatment technologies of water reverse osmosis concentrates. *Water Research*, *46*(2), 267–283. https://doi.org/10.1016/j.watres.2011.10.046

Picard, T., Cathalifaud-Feullade, G., Mazet, M., & Vandensteendam, C. (2000). Cathodic dissolution in the electrocoagulation process using aluminum electrodes, 77–80.

Ramachandran, K. M., & Tsokos, C. P. (2015). Chapter 9 - Design of Experiments. In *Mathematical Statistics with Applications in R (Second Edition)* (pp. 459–494). Boston: Academic Press. Retrieved from http://www.sciencedirect.com/science/article/pii/B9780124171138000096

Ricordel, J. C., Darchen, A., & Hadjiev, D. (2010). Electrocoagulation–electroflotation as a surface water treatment for industrial uses, Sep. Purif. Technol. 74, 342–347.

Sasane, K. S., & Korke, S. R. (2015). Treatment of Distillery wastewater by Electrocoagulation using Aluminum electrodes. *International Journal of Modern Trends in Engineering and Research*.

Sauvet-Goichon, B. (2007). Ashkelon desalination plant — A successful challenge. *Desalination*, *203*(1–3), 75–81. https://doi.org/10.1016/j.desal.2006.03.525

Sayyaadi, H., Saffari, A., & Mahmoodian, A. (2010). Various approaches in optimization of multi effects distillation desalination systems using a hybrid meta-heuristic optimization tool. *Desalination*, *254*(1–3), 138–148. https://doi.org/10.1016/j.desal.2009.11.045

Semiat, R. (2000). Multi-effect distillation (MED). Retrieved from http://www.eolss.net/Sample-Chapters/C07/E6-144-44-00.pdf

Shafaei, A., Pajootan, E., Nikazar, M., & Arami, M. (2011). Removal of Co(II) from aqueous solution by electrocoagulation process using aluminum electrodes. *Desalination*, *279*, 121–126.

Shafaei, A., Rezayee, M., Arami, M., & Nikazar, M. (2010). Removal of Mn2+ ions from synthetic wastewater by electrocoagulation process, Desalination 260, 23–28.

Shatat, M., & Riffat, S. B. (2012). Water desalination technologies utilizing conventional and renewable energy sources. *International Journal of Low-Carbon Technologies*, cts025. https://doi.org/10.1093/ijlct/cts025

Song, C., Kitamura, Y., & Li, S. (2014). Optimization of a novel cryogenic CO_2 capture process by response surface methodology (RSM). *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1666–1676. https://doi.org/10.1016/j.jtice.2013.12.009

Tanuwidjaja, D. (2002). Experimental investigation on rejection of Sodium Sulfate by reverse osmosis membranes. Retrieved from http://www.seas.ucla.edu/stenstro/t/t28.pdf

Tezcan Un, U., Ugur, S., Koparal, A. S., & Bakir Ogutveren, U. (2006). Electrocoagulation of olive mill wastewaters, Sep. Purif. Technol. 52, 136–141.

Tian, Y., He, W., Zhu, X., Yang, W., Ren, N., & Logan, B. E. (2016). Energy efficient electrocoagulation using an air-breathing cathode to remove nutrients from wastewater. *Chemical Engineering Journal*, *292*, 308–314. https://doi.org/10.1016/j.cej.2016.02.004

Tir, M., & Moulai-Mostefa. (2008). Optimization of oil removal from oily wastewater by electrocoagulation using response surface method, J. Hazard. Mater. 158, 107–115.

Uduman, N., Bourniquel, V., Danquah, M. K., & Hoadley, A. F. . (2011). A parametric study of electrocoagulation as a recovery process of marine microalgae for biodiesel production, Chem. Eng. J. 174, 249–257.

Ueda, T., Wakitani, K., & Nanasawa, A. (2012). Influence of electrolyte temperature on efficiency of electrochemical chloride removal from concrete. *Electrochimica Acta*, *86*, 23–27. https://doi.org/10.1016/j.electacta.2012.05.026

Vepsäläinen, M., & Valtion teknillinen tutkimuskeskus. (2012). *Electrocoagulation in the treatment of industrial waters and wastewaters*.

voutchkov, N. (2017, August 17). Desalination – Past, Present and Future. Retrieved from http://www.iwa-network.org/desalination-past-present-future/

Wang, Y., Guo, X., Li, J., Yang, Y., Lei, Z., & Zhang, Z. (2012). Efficient Electrochemical Removal of Ammonia with Various Cathodes and Ti/RuO₂-Pt Anode. *Open Journal of Applied Sciences*, *2*(4), 241–247. https://doi.org/10.4236/ojapps.2012.24036

Water for a sustainable world includes data and indicators annex for water and energy. (2015). Paris: Unesco.

Wu, J. J., Wu, C.-C., Ma, H.-W., & Chang, C.-C. (2004). Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere*, *54*(7), 997–1003. https://doi.org/10.1016/j.chemosphere.2003.10.006

Yetilmezsoy, K., Ilhan, F., Sapci-Zengin, Z., Sakar, S., & Gonullu, M. T. (2009). Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: A post-treatment study, J. Hazard. Mater. 162, 120–132.

Yilmaz, A. E., Boncukcuoglu, R., Kocakerim, M. M., Yilmaz, M. T., & Paluluoglu, C. (2008). Boron removal from geothermal waters by electrocoagulation, J. Hazard. Mater. 153, 146–151.

Zhu, J., Zhao, H., & Ni, j. (2007). Fluoride distribution in electrocoagulation defluoridation process, Sep. Purif. Technol. 56, 184–191.

Appendix

Table A1: Effect of no current density on the percentage of removal of NH_4^+ after 6 hours at different temperature and an initial NH_4^+ Concentrations of 14250 mg/l

Temperature(°C)	% removal of NH_4^+	% removal of NH_4^+	% removal of NH_4^+ (Avg)	%removal of NH_4^+ (SD)	current density
20	12.2	12.8	12.5	0.42	0 A/cm^2
30	13.04	12.43	12.735	0.43	0 A/cm^2
TTEST(1-2)	0.63				

Table A2: Effect of current density on the percentage of removal of NH_4^+ after 6 hours at different temperature and an initial NH_4^+ Concentrations of 14250 mg/l

Temperature(°C)	% removal of NH_4^+	% removal of NH_4^+	% removal of NH_4^+ (Avg)	%removal of NH_4^+ (SD)	current density
20	45.6	46.2	45.9	0.42	0.1167 A/cm^2
30	70.5	72.6	71.55	1.48	0.1167 A/cm^2

Table A3: Effect of no current density on the percentage of removal of Cl^- after 6 hours at different temperature and an initial Cl^- Concentrations of 20000 mg/l

Temperature(°C)	% removal of Cl^-	% removal of Cl^-	% removal of Cl^- (Avg)	%removal of Cl^- (SD)	current density
20	3.9	3.2	3.55	0.49	0 A/cm^2
30	5.8	3.8	4.8	1.41	0 A/cm^2
TTEST(1-2)	0.35				

Table A4: Effect of current density on the percentage of removal of Cl^- after 6 hours at different temperature and an initial Cl^- Concentrations of 20000 mg/l

Temperature(°C)	% removal of Cl^-	% removal of Cl^-	% removal of Cl^- (Avg)	%removal of Cl^- (SD)	current density
20	26.36	25.39	25.875	0.68	0.1167 A/cm^2
30	27.77	25.99	26.88	1.25	0.1167 A/cm^3

Table A5: Effect of current density on the percentage removal of NH_4^+ ions after 6 hours at 20°C and initial concentrations of 14250 mg/l of NH_4^+.

Current Density(A/cm2)	% removal of NH_4^+	% removal of NH_4^+	% removal of NH_4^+ (Avg)	%removal of NH_4^+ (SD)	Temperature(°C)
0	12.2	12.8	12.5	0.42	20
0.033	44.91	45.76	45.33	0.59	20
0.1167	45.69	46.23	45.96	0.38	20
0.2	64.81	68.51	66.66	2.61	20
TTEST(0-1)	0.000248				
TTEST(1-2)	0.33				
TTEST(2-3)	0.0080				

Table A6: Effect of current density on the percentage removal of Cl^- ions after 6 hours at 20°C and initial concentrations of 20000 mg/l of Cl^-

Current Density(A/cm2)	% removal of Cl^-	% removal of Cl^-	% removal of Cl^- (Avg)	% removal of Cl^- (SD)	Temperature (°C)
0	3.9	3.2	3.55	0.49	20
0.033	22.92	22.67	22.80	0.17	20
0.1167	26.36	25.39	25.87	0.68	20
0.2	28.95	27.79	28.37	0.82	20
TTEST (0-1)	0.000372964				
TTEST (1-2)	0.025597481				
TTEST (2-3)	0.080522843				

Table A7: Effect of current density on the rate of removal of NH_4^+ ions at 20°C and initial concentrations of 14250 mg/l of NH_4^+.

Current Density(A/cm^2)	Rate of removal of NH_4^+	Rate of removal of NH_4^+	Rate of removal of NH_4^+ (Avg)	Rate of removal of NH_4^+ (SD)	Temperature (°C)
0	2.03	2.13	2.08	0.070710678	20
0.033	12.85310734	11.44067797	12.14689266	0.998738392	20
0.1167	14.4927	13	13.74635	1.055498292	20
0.2	17.59259259	19.44444444	18.51851852	1.309457002	20
TTEST(0-1)	0.004909606				
TTEST(1-2)	0.259845051				
TTEST(2-3)	0.056860607				

Table A8: Effect of current density on the rate of removal of Cl^{-1} ions at 20°C and initial concentrations of 20000 mg/l of Cl^{-1}

Current Density(A/cm^2)	% removal of Cl^{-1}	% removal of Cl^{-1}	% removal of Cl^{-1} (Avg)	% removal of Cl^{-1}(SD)	Temperature (°C)
0	0.65	0.53	0.59	0.084852814	20
0.033	4.0762	5.246	4.6611	0.827173513	20
0.1167	4.4149	5.536	4.97545	0.792737412	20
0.2	5.0417	6.722	5.88185	1.188151524	20
TTEST(0-1)	0.020227902				
TTEST(1-2)	0.735406923				
TTEST(2-3)	0.46419344				